

Case Nos. 2022-1855; 2022-2151

**IN THE
UNITED STATES COURT OF APPEALS
FOR THE FEDERAL CIRCUIT**

TERVES LLC,
Plaintiff-Appellee

v.

YUEYANG AEROSPACE NEW MATERIALS CO. LTD.,
Defendant

ECOMETAL INC., NICK YUAN,
Defendants-Appellants

On Appeal from

United States District Court Northern District of Ohio
Judge Donald C. Nugent (Case No. 1:19-Cv-1611-DCN)

CORRECTED APPELLANTS' PRINCIPAL BRIEF

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PATENT CLAIMS AT ISSUE

U.S. Patent No. 10,329,653 B2

Independent Claims:

1. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material having a greater melting point temperature than a solidus temperature of said magnesium, said additive material constituting about 0.05 wt. %-45 wt. % of said mixture, said additive material forming precipitant in said magnesium composite, said additive material includes one or more metals selected from the group consisting of copper, nickel, iron, and cobalt, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

12. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite comprising a mixture of a magnesium or a magnesium alloy and an additive material, said additive material having a greater melting point temperature than a solidus temperature of said magnesium, said composite including greater than 50 wt. % magnesium, said additive material constituting about 0.05-45 wt. % of said magnesium composite, said additive material having a melting point temperature that is 100° C. greater than a melting temperature of said magnesium or magnesium alloy, said additive material including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium, and iron, at least a portion of said additive material remaining unalloyed additive material, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that includes said unalloyed additive material, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

25. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising at least 85 wt. % magnesium; one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel,

cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

29. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.01-1 wt. % zirconium; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

33. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.5-10 wt. % aluminum; 0.05-6 wt. % zinc; 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

37. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.05-6 wt. % zinc; 0.01-1 wt. % zirconium; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

41. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising over 50 wt. % magnesium; one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel and cobalt, said

magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

45. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising over 50 wt. % magnesium; one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002- 0.04 wt. % boron, and 0.4-0.7 wt. % bismuth; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, and cobalt, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/ hr. in 3 wt. % KCl water mixture at 90° C.

49. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting about 0.05-45 wt. % of said mixture, said additive material includes one or more metals selected from the group consisting of copper, nickel, titanium, iron, and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said additive material located in sufficient quantities in said galvanically-active intermetallic phases so as to obtain a composition and morphology of said galvanically-active intermetallic phases such that a galvanic corrosion rate along said galvanically-active intermetallic phases causes said magnesium composite to have a dissolution rate of at least at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

74. A dissolvable magnesium composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium composite includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting at least 0.1 wt. % of said mixture, said magnesium in said magnesium composite constituting at least 85 wt. %, said additive material is a metal material selected from the group consisting of copper, nickel and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said magnesium composite has a dissolution rate of 84-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

Dependent Claims:

2. The magnesium composite as defined in claim 1, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.
3. The magnesium composite as defined in claim 1, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %.
4. The magnesium composite as defined in claim 1, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.
5. The magnesium composite as defined in claim 1, wherein said additive material includes copper, said copper constitutes about 0.05-35 wt. % of said magnesium composite, said copper forms galvanically-active in situ precipitate in said magnesium composite.
7. The magnesium composite as defined in claim 1, where said magnesium composite is subjected to a deformation processing to reduce grain size of said magnesium composite, increase tensile yield strength of said magnesium composite, increase elongation of said magnesium composite, or combinations thereof.
9. The magnesium composite as defined in claim 1, wherein a dissolution rate of said magnesium composite is about 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.
13. The magnesium composite as defined in claim 12, wherein said additive material is added to said magnesium or magnesium alloy while said magnesium or magnesium alloy is at a temperature that is above said solidus temperature of said magnesium and a temperature that is less than a melting point of said additive material to form said mixture.
14. The magnesium composite as defined in claim 13, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about

0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %.

15. The magnesium composite as defined in claim 14, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

18. The magnesium composite as defined in claim 15, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

19. The magnesium composite as defined in claim 12, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %.

20. The magnesium composite as defined in claim 12, said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

23. The magnesium composite as defined in claim 12, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

26. The dissolvable magnesium alloy composite as defined in claim 25, wherein a dissolution rate of said magnesium alloy composite is 100-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

27. The dissolvable magnesium composite as defined in claim 25, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

30. The dissolvable magnesium alloy composite as defined in claim 29, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

31. The dissolvable magnesium composite as defined in claim 29, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

34. The dissolvable magnesium alloy composite as defined in claim 33, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

35. The dissolvable magnesium composite as defined in claim 33, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

38. The dissolvable magnesium alloy composite as defined in claim 37, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

39. The dissolvable magnesium composite as defined in claim 37, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

42. The dissolvable magnesium alloy composite as defined in claim 41, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

43. The dissolvable magnesium composite as defined in claim 41, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

46. The dissolvable magnesium alloy composite as defined in claim 45, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

47. The dissolvable magnesium composite as defined in claim 45, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

50. The magnesium composite as defined in claim 49, wherein said additive material includes one or more metals selected from the group consisting of copper, nickel, and cobalt.

52. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

53. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in an amount of about 0.1-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in an amount of about 0.0002- 0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %.

54. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in an amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in an amount of about 0.0002- 0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %.

55. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes at least 85 wt. % magnesium, and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese.

56. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes 60-95 wt. % magnesium and 0.01-1 wt. % zirconium.

57. The magnesium composite as defined in claim 56, wherein said magnesium alloy further includes 0.05-6 wt. % zinc.

58. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes 60-95 wt. % magnesium, 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, and 0.15-2 wt. % manganese.

59. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group

consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, is 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese.

60. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

61. The magnesium composite as defined in claim 49, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

64. The magnesium composite as defined in claim 49, wherein said additive material includes copper, said copper constitutes about 0.05-35 wt. % of said magnesium composite, said copper forms the galvanically-active in situ precipitate in said magnesium composite.

66. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is about 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

67. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

69. The magnesium composite as defined in claim 49, wherein said additive material has a melting point temperature that is 100° C. greater than a melting temperature of said magnesium or magnesium alloy.

70. The magnesium composite as defined in claim 49, wherein said magnesium composite is at least partially included in a down hole well component, said down hole well component including one or more components selected from the group consisting of a sleeve, frac ball, hydraulic actuating tooling, tube, valve, valve component, or plug.

76. The magnesium composite as defined in claim 74, wherein said additive material includes nickel, a content of said nickel in said magnesium composite is at least 0.3 wt. %.

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Independent Claims:

2. A dissolvable magnesium composite that at least partially forms a ball, a frac ball, a tube, a plug or other tool component that is to be used in a well drilling or completion operation, said dissolvable magnesium composite includes in situ precipitate, said dissolvable magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said magnesium composite includes greater than 50 wt. % magnesium, said in situ precipitate includes said additive material, said additive material includes one or more metal materials selected from the group consisting of a) copper wherein said copper constitutes 0.1-35 wt. % of said dissolvable magnesium composite, b) wt. % nickel wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium composite, and c) cobalt wherein said cobalt constitutes 0.1-20 wt.% of said dissolvable magnesium composite, said dissolvable magnesium composite has a dissolution rate of at least 75 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.

19. A dissolvable magnesium cast composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material includes one or more metals selected from the group consisting of a) copper wherein said copper constitutes at least 0.01 wt. % of said dissolvable magnesium cast composite, b) nickel wherein said nickel constitutes at least 0.01 wt. % of said dissolvable magnesium cast composite, and c) cobalt wherein said cobalt constitutes at least 0.01 wt. % of said dissolvable magnesium cast composite, said magnesium composite includes in situ precipitate, said in situ precipitate includes said additive material, a plurality of particles of said in situ precipitate having a size of no more than 50 µm, said magnesium composite has a dissolution rate of at least 5 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.

94. A dissolvable magnesium cast composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material includes a) nickel wherein said nickel constitutes 0.01-5 wt. % of said dissolvable magnesium cast composite or b) nickel wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite, said dissolvable magnesium cast composite includes in situ precipitate, said in situ precipitate includes said additive material, said dissolvable magnesium cast composite has a dissolution rate of at least 75 mg/cm² / hr. in 3 wt. % KCl water mixture at 90° C.

Dependent Claims:

3. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 75-325 mg/cm²/hr. in 3 wt.% KCl water mixture at 90° C.
4. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 84-325 mg/cm² /hr. in 3 wt.% KCl water mixture at 90° C.
5. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 100-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.
8. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium alloy comprises greater than 40 than 50 wt. % magnesium and no more than 10 wt. % aluminum, and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt.% zirconium, and 0.15-2 wt.% manganese.
9. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and no more than 10 wt. % aluminum, and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.05-1 wt. % zirconium, 0.05-0.25 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.
10. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes nickel.
11. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes nickel, said nickel constitutes 0.3-0.7 wt. % of said dissolvable magnesium composite.
13. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes copper.
16. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium content in said dissolvable magnesium composite is at least 75 wt. %.

17. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium content in said dissolvable magnesium composite is at least 85 wt. %.
20. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium composite includes at least 85 wt. % magnesium.
21. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium composite has a dissolution rate of at least 40 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.
22. The dissolvable magnesium cast composite as defined in claim 20, wherein said magnesium composite has a dissolution rate of at least 40 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.
23. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium composite includes no more than 10 wt. % aluminum.
24. The dissolvable magnesium cast composite as defined in claim 20, wherein said magnesium composite includes no more than 10 wt. % aluminum.
25. The dissolvable magnesium cast composite as defined in claim 21, wherein said magnesium composite includes no more than 10 wt. % aluminum.
26. The dissolvable magnesium cast composite as defined in claim 22, wherein said magnesium composite includes no more than 10 wt. % aluminum.
27. The dissolvable magnesium cast composite as defined in claim 23, wherein said magnesium composite includes at least 50 wt. % magnesium.
28. The dissolvable magnesium cast composite as defined in claim 25, wherein said magnesium composite includes at least 50 wt. % magnesium.
29. The dissolvable magnesium cast composite as defined in claim 19, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.
30. The dissolvable magnesium cast composite as defined in claim 20, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.

31. The dissolvable magnesium cast composite as defined in claim 22, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.

32. The dissolvable magnesium cast composite as defined in claim 23, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm²/hr. in 3 wt. 5 % KCl water mixture at 90° C.

33. The dissolvable magnesium cast composite as defined in claim 27, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.

34. The dissolvable magnesium cast composite as defined in claim 28, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.

35. The dissolvable magnesium cast composite as defined wt. % manganese. in claim 27, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

36. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

37. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt. %, zinc in an amount of 0.1-6 wt.%, zirconium in an amount 30 of 0.01-3 wt.%, manganese in an amount of 0.15-2 wt.%, boron in an amount of 0.0002-0.04 wt.%, and bismuth in an amount of 0.4-0.7 wt. %.

38. The dissolvable magnesium cast composite as defined 35 in claim 28, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt.%, zinc in an amount of 0.1-6 wt.%, zirconium in an amount of 0.01-3 wt.%, manganese in an amount of 0.15-2 wt.%, boron in an amount of 0.0002-0.04 wt.%, and bismuth in an amount of 0.4-0.7 wt. %.

39. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt.%, zinc in an amount of 0.1-3 wt.%, zirconium in an amount of 0.01-1 wt.%, manganese in an amount of 0.15-2 wt.%, boron in an amount of 0.0002-0.04 wt. %, and bismuth in amount of 0.4-0.7 wt. %.

40. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt.%, zinc in an amount of 0.1-3 wt.%, zirconium in an amount of 0.01-1 wt.%, manganese in an amount of 0.15-2 wt.%, boron in an amount of 0.0002-0.04 wt. %, and bismuth in amount of 0.4-0.7 wt. %.

41. The dissolvable magnesium cast composite as defined in claim 20, wherein said magnesium alloy includes at least 85 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese.

42. The dissolvable magnesium cast composite as defined in claim 22, wherein said magnesium alloy includes at least 85 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt.% zirconium, and 0.15-2 wt.% manganese.

43. The dissolvable magnesium cast composite as defined in claim 23, wherein said magnesium alloy includes at least 85 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt.% zirconium, and 0.15-2 wt.% manganese.

44. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese.

45. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt.% zinc, 0.01-1 wt.% zirconium, and 0.15-2 wt. % manganese.

46. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy comprises greater than 59 wt. % magnesium and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.05-1 wt. % zirconium, 0.05-0.25 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

47. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.05-1 wt. % zirconium, 0.05-0.25 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

51. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium alloy includes over 50 wt. % magnesium and one or metals selected from the group consisting of 0.1-3 wt. % zinc, 0.1-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

52. The dissolvable magnesium cast composite as defined in claim 19, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

53. The dissolvable magnesium cast composite as defined in claim 20, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

54. The dissolvable magnesium cast composite as defined in claim 22, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

55. The dissolvable magnesium cast composite as defined in claim 23, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

56. The dissolvable magnesium cast composite as defined in claim 27, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

57. The dissolvable magnesium cast composite as defined 5 in claim 28, wherein said wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

58. The dissolvable magnesium cast composite as defined in claim 19, wherein said additive material includes copper, said copper constitutes 0.01-35 wt. % of said dissolvable magnesium cast composite.

59. The dissolvable magnesium cast composite as defined in claim 20, wherein said additive material includes copper, said copper constitutes 0.01-35 wt. % of said dissolvable magnesium cast composite.

60. The dissolvable magnesium cast composite as defined in claim 22, wherein said additive material includes copper, said copper constitutes 0.01-35 wt. % of said dissolvable magnesium cast composite.

61. The dissolvable magnesium cast composite as defined in claim 23, wherein said additive material includes copper, said copper constitutes 0.01-35 wt. % of said dissolvable magnesium cast composite.

62. The dissolvable magnesium cast composite as defined in claim 17, wherein said additive material includes copper, said copper constitutes 0.01-35 wt. % of said dissolvable magnesium cast composite.

63. The dissolvable magnesium cast composite as defined in claim 28, wherein said additive material includes copper, said copper constitutes 0.01-35 wt. % of said dissolvable magnesium cast composite.

64. The dissolvable magnesium cast composite as defined in claim 19, wherein said additive material includes copper, said copper constitutes 0.5-15 wt. % of said dissolvable magnesium cast composite.

65. The dissolvable magnesium cast composite as defined in claim 20, wherein said additive material includes copper, said copper constitutes 0.5-15 wt. % of said dissolvable magnesium cast composite.

66. The dissolvable magnesium cast composite as defined in claim 22, wherein said additive material includes copper, said copper constitutes 0.5-15 wt. % of said dissolvable magnesium cast composite.

67. The dissolvable magnesium cast composite as defined in claim 23, wherein said additive material includes copper, said copper constitutes 0.5-15 wt. % of said dissolvable magnesium cast composite.

68. The dissolvable magnesium cast composite as defined in claim 27, wherein said additive material includes copper, said copper constitutes 0.5-15 wt. % of said dissolvable magnesium cast composite.

69. The dissolvable magnesium cast composite as defined in claim 28, wherein said additive material includes copper, said copper constitutes 0.5-15 wt. % of said dissolvable magnesium cast composite.

76. The dissolvable magnesium cast composite as defined in claim 19, wherein said additive material includes one or more metal materials selected from the group consisting of 0.1-35 wt. % copper, 0.1-24.5 wt. % nickel and 0.1-20 wt. % cobalt.

77. The dissolvable magnesium cast composite as defined in claim 29, wherein said additive material includes one or more metal materials selected from the group consisting of 0.1-35 wt. % copper, 0.1-24.5 wt. % nickel and 0.1-20 wt. % cobalt.

78. The dissolvable magnesium cast composite as defined in claim 22, wherein said additive material includes one or more metal materials selected from the group consisting of 0.1-35 wt. % copper, 0.1-24.5 wt. % nickel and 0.1-20 wt. % cobalt.

79. The dissolvable magnesium cast composite as defined in claim 23, wherein said additive material includes one or more metal materials selected from the group consisting of 0.1-35 wt. % copper, 0.1-24.5 wt. % nickel and 0.1-20 wt. % cobalt.

80. The dissolvable magnesium cast composite as defined in claim 27, wherein said additive material includes one or more metal materials selected from the group consisting of 0.1-35 wt. % copper, 0.1-24.5 wt. % nickel and 0.1-20 wt. % cobalt.

81. The dissolvable magnesium cast composite as defined in claim 28, wherein said additive material includes one or more metal materials selected from the group consisting of 0.1-35 wt. % copper, 0.1-24.5 wt. % nickel and 0.1-20 wt. % cobalt.

82. The dissolvable magnesium cast composite as defined in claim 19, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

83. The dissolvable magnesium cast composite as defined in claim 20, wherein said dissolvable magnesium cast composite has one or more properties selected from the

group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

84. The dissolvable magnesium cast composite as defined in claim 22, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

85. The dissolvable magnesium cast composite as defined in claim 25, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

86. The dissolvable magnesium cast composite as defined in claim 27, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

87. The dissolvable magnesium cast composite as defined in claim 28, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

88. The dissolvable magnesium cast composite as defined in claim 19, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

89. The dissolvable magnesium cast composite as defined in claim 20, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

90. The dissolvable magnesium cast composite as defined in claim 22, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

91. The dissolvable magnesium cast composite as defined in claim 23, wherein said dissolvable magnesium cast composite has one or more properties selected from the

group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

92. The dissolvable magnesium cast composite as defined in claim 27, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

93. The dissolvable magnesium cast composite as defined in claim 28, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

95. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium cast composite includes no more than 10 wt. % aluminum.

96. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium composite cast includes at least 85 wt. % magnesium.

97. The dissolvable magnesium cast composite as defined in claim 95, wherein said dissolvable magnesium cast composite includes at least 85 wt. % magnesium.

98. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium cast composite has a dissolution rate of 75-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C.

99. The dissolvable magnesium cast composite as defined in claim 97, wherein said dissolvable magnesium cast composite has a dissolution rate of 75-325 mg/cm² /hr. in 3 wt. % KCl water mixture at 90° C

100. The dissolvable magnesium cast composite as defined in claim 94, wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

101. The dissolvable magnesium cast composite as defined in claim 99, wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

102. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

103. The dissolvable magnesium cast composite as defined in claim 101, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

FORM 9. Certificate of Interest

Form 9 (p. 1)
July 2020

**UNITED STATES COURT OF APPEALS
FOR THE FEDERAL CIRCUIT**

CERTIFICATE OF INTEREST

Case Number 2022-1855

Short Case Caption Terves LLC v. Ecometal Inc

Filing Party/Entity Ecometal Inc. and Nick Yuan

Instructions: Complete each section of the form. In answering items 2 and 3, be specific as to which represented entities the answers apply; lack of specificity may result in non-compliance. **Please enter only one item per box; attach additional pages as needed and check the relevant box.** Counsel must immediately file an amended Certificate of Interest if information changes. Fed. Cir. R. 47.4(b).

I certify the following information and any attached sheets are accurate and complete to the best of my knowledge.

Date: 06/08/2022

Signature: /s/ Martin S. High

Name: Martin S. High

FORM 9. Certificate of Interest

Form 9 (p. 2)
July 2020

1. Represented Entities. Fed. Cir. R. 47.4(a)(1).	2. Real Party in Interest. Fed. Cir. R. 47.4(a)(2).	3. Parent Corporations and Stockholders. Fed. Cir. R. 47.4(a)(3).
Provide the full names of all entities represented by undersigned counsel in this case.	Provide the full names of all real parties in interest for the entities. Do not list the real parties if they are the same as the entities. <input checked="" type="checkbox"/> None/Not Applicable	Provide the full names of all parent corporations for the entities and all publicly held companies that own 10% or more stock in the entities. <input checked="" type="checkbox"/> None/Not Applicable
Ecometal Inc.		
Nick Yuan		

☐ Additional pages attached

FORM 9. Certificate of Interest

Form 9 (p. 3)
July 2020

4. Legal Representatives. List all law firms, partners, and associates that (a) appeared for the entities in the originating court or agency or (b) are expected to appear in this court for the entities. Do not include those who have already entered an appearance in this court. Fed. Cir. R. 47.4(a)(4).

☐ None/Not Applicable

☐ Additional pages attached

Edward L. White of Edward L. White PC	Rachel N. Byrnes of Nelson Mullins Riley & Scarborough	John Q. Lewis of Nelson Mullins Riley & Scarborough
Charles C. Weddle , III of White & Weddle	Joe E. White , Jr. of White & Weddle	Evan W. Talley of Dunlap Coddling
Jordan A. Sigale of Dunlap Coddling	Steven J. Forbes of Norchi Forbes	

5. Related Cases. Provide the case titles and numbers of any case known to be pending in this court or any other court or agency that will directly affect or be directly affected by this court's decision in the pending appeal. Do not include the originating case number(s) for this case. Fed. Cir. R. 47.4(a)(5). See also Fed. Cir. R. 47.5(b).

☐ None/Not Applicable

☐ Additional pages attached

Magnesium Machine LLC v. Terves LLC (5:21-cv-01115-PRW, OKWD)		

6. Organizational Victims and Bankruptcy Cases. Provide any information required under Fed. R. App. P. 26.1(b) (organizational victims in criminal cases) and 26.1(c) (bankruptcy case debtors and trustees). Fed. Cir. R. 47.4(a)(6).

☒ None/Not Applicable

☐ Additional pages attached

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STATEMENT OF RELATED CASES

In accordance with Federal Circuit Rule 47.5(a), Appellants state that Case No. 22-2151 is a related case that has been consolidated with this appeal. This opening brief addresses the issues raised in the Notice of Appeal filed in Case No. 22-2151. Appellants are not aware of any other appeal in or from the same civil action or proceeding in the lower court that was previously before this Court or any other appellate court other than the actions consolidated herein.

JURISDICTIONAL STATEMENT

The United States District Court for the Northern District of Ohio had jurisdiction in this patent infringement case pursuant to 28 U.S.C. § 1331 and 1338(a). On April 12, 2022, the District Court granted in part and denied in part Terves' motion for summary judgment as to liability for patent infringement and granted in part and denied in part Appellants' motion for summary judgment. [Appx00001–00019.] Following a jury trial and verdict on Terves' claim of patent infringement, the District Court entered a final judgment on April 28, 2022. [Appx00020–00022.] Appellants, on May 26, 2022, timely filed a notice of appeal of the District Court's entry of final judgment. [App. Dkt 1.] On July 20, 2022, the District Court entered a permanent injunction against Appellants and non-party Magnesium Machine LLC. [Appx00023–00030.] On August 15, 2022, Appellants timely filed a notice of appeal of the District Court's entry of a permanent injunction. On September 8, 2022, this Court ordered that both appeals be consolidated. [App. Dkt 14.] This Court has jurisdiction over both appeals under 28 U.S.C. § 1295(a)(1).

STATEMENT OF THE ISSUES

1. Whether the trial court erred in granting summary judgment in favor of Terves when it held that Terves' '653 and '740 Patents were valid and patentable and that Appellants' accused products infringed those claims.
2. Whether the trial court erred in denying Nick Yuan's Motion for Directed Verdict regarding his personal liability and thereafter including him on the verdict form, where Terves did not elicit any evidence regarding Mr. Yuan's personal liability at trial.
3. Whether the trial court erred in entering a permanent injunction against Ecometal Inc. and Nick Yuan and also in prohibiting non-party Magnesium Machine from purchasing certain infringing materials.

STATEMENT OF THE CASE

I. Factual Background

A. The Xiao Patent

On July 8, 2013, Xiao Daihong filed for and later secured a patent in China (hereinafter referred to as the “Xiao patent”). [Appx12850–12866.] The Xiao patent relates to a dissolvable magnesium alloy. Notably, the abstract of disclosures on the very first page of the Xiao patent states:

A light and pressure-proof fast-decomposed cast magnesium alloy can be used as a tripping ball material for a multi-stage sliding sleeve staged fracturing technique. The light and pressure-proof fast-decomposed cast magnesium alloy is composed of the following components: 13 to 25% of Al, 2 to 15% of Zn, 0.1 to 5% of Fe, 0.05 to 5% of Cu, 0.05 to 5% of Ni, 0 to 5% of Ag, 0.05 to 0.5% of Zr, 0.05 to 0.5% of Ti, and the remainder is Mg. The preparation method comprises the following steps: weighing the respective components according to the designed component proportions of the magnesium alloy; then first loading pure magnesium and pure aluminum into a smelting furnace, next loading pure zinc and an intermediate alloys of the other components into a magnesium-aluminum alloy melt after melting; increasing the temperature for melting, refining, degassing, waiting for a while and then casting in a protective atmosphere. The light and pressure-proof fast-decomposed cast magnesium alloy of the present invention is reasonable in component ratio, and simple in the production process; the light and pressure-proof fast-decomposed cast magnesium alloy can be obtained by controlling the components of the alloy; the alloy decomposition performance exceeds that of a traditional cast magnesium alloy; the demands of the multi-stage sliding sleeve staged-fracturing technique on the decomposition performance of the tripping ball material can be met; industrialized application can be achieved; application of the magnesium alloy in the field of exploitation of petroleum and gas is thus expanded.

[Appx12850–12851.] The Xiao patent was published on October 9, 2013. In or around August 2019, Nick Yuan purchased the Xiao patent and still owns this patent to date. [Appx12131.]

B. Ecometal’s Business

Ecometal is a Canadian company owned by Nick Yuan, who is a Canadian permanent resident. [Appx12082.] Ecometal is a broker of specialty metals including aluminum, magnesium, and rare earth metals. [Appx12089–12090.] Ecometal connects purchasers having a need for metal alloys with manufacturers who have alloys that may satisfy the needs of the purchasers. [Appx12090–12092.] Typically, the manufacturers with whom Ecometal connects are in China. [Appx12090.]

Non-party Magnesium Machine, LLC (aka Magnesium Machine Parts or “MMP”) is an Oklahoma company that purchased magnesium alloys, most of which are dissolvable in water or salt solutions, in transactions brokered by Ecometal. [Appx12100.] MMP machines or arranges for the machining of the metal it previously purchased from Ecometal and the assembly of machined metal components and other materials into balls and plugs used in fracking oil and gas wells. [Appx12092.]

Ecometal and MMP entered into an exclusive manufacturing agreement in or around June 2016 whereby Ecometal agreed to broker the importation of certain magnesium alloys from China to MMP. [Appx12834–12845.] Under this agreement,

Ecometal was acting “solely as a contract manufacturer”; in fact, the agreement explicitly states that the parties were not forming a joint venture or association of any type. [Appx12836.]

C. The Terves Patents

Terves is a Euclid, Ohio company that manufactures and sells a family of dissolvable magnesium products—both cast magnesium and fracking tools—under the *TervAlloy* brand name. [Appx11767.] Terves owns a series of U.S. patents in the field of dissolvable magnesium. A timeline of the patent applications and issuance is below:

- *April 18, 2014* – Terves filed U.S. Provisional Application No. 61/981,425 (the “‘425 Provisional”). [Appx04458.]
- *April 17, 2015* – Terves filed the U.S. application 14/689,295, claiming priority based on the ‘425 Provisional, that issued as U.S. Pat. 9,903,010 (the “‘010 Patent”) on Feb. 27, 2018.¹ [Appx04459.]
- *July 5, 2017* – Terves filed the U.S. application 15/641,439, as a divisional patent application of the application for the ‘010 Patent, that issued on June 25, 2019 as U.S. Pat. 10,329,653 B2 (the “‘653 Patent”). This patent relates to a method of manufacture for dissolvable magnesium.² [Appx04482.]
- *August 11, 2017* – Terves filed a Chinese patent application corresponding to the ‘010 Patent, and the Chinese Patent Office rejected the claims based primarily on Xiao. [Appx04570.] Terves was able to overcome the rejection

¹ The District Court determined that claims originally brought by Terves under the ‘010 Patent were dismissed with prejudice. That dismissal is not at issue in this appeal.

² At trial, evidence showed that representatives of Terves contacted Ecometal in 2015 (before the ‘653 or ‘740 patent applications were submitted) to obtain Ecometal’s list of master alloy formulations. [See Appx12867–12874.]

by amending its claims to include a process limitation not applicable to the product claims of the ‘653 and later-filed ‘740 Patents.

- *October 12, 2018* – Terves filed the U.S. application 16/158,915, as a continuation-in-part of the application for the ‘653 patent, that issued on Jun. 23, 2020 as U.S. Pat. 10,689,740 (the “‘740 Patent”).³ [Appx04502.]

All of Terves’ patent applications were filed *after* the Xiao patent application was filed and published.

On September 11, 2020 Ecometal filed with the USPTO a request for *inter partes* review of the ‘653 patent. [Appx12071.] Ecometal asserted that the Xiao patent was prior art and Terves’ ‘653 patent was invalid. This request was denied as being untimely filed by prior counsel rather than determined on its merits.⁴ [*Id.*] On July 7, 2021, Ecometal filed with the USPTO a request for *ex parte* reexamination of the ‘653 patent, and the USPTO ordered a reexamination on July 26, 2021 finding a substantial question of patentability. [Appx12875.] On November 19, 2021, the USPTO issued a non-final office action rejecting all of the claims in Terves’ ‘653 patent as invalid and unpatentable in view of the Xiao patent. [Appx12875–13050.] The reexamination was later resolved in Terves’ favor by the USPTO on March 28, 2022, finding *inter alia* that “[t]here is no suggestion from [the] Xaio [patent] to

³ The ‘653 and ‘740 patents will be referred to collectively as “Terves’ patents.”

⁴ Appellants filed a malpractice action against prior counsel on August 12, 2022 for missing the one-year deadline in which to file the petition for *inter partes* review.

substitute copper, nickel, iron or cobalt for the aluminum in the galvanically-active intermetallic.” [Appx12826–12830.]

D. Expert Opinions

Both Terves and Appellants retained patent experts in this case, each of whom offered validity and infringement opinions.

Terves retained Dr. Lee Swanger. Regarding validity, Dr. Swanger opined in his expert report that Terves’ patent claims were neither anticipated by nor obvious in view of prior art, particularly the Xiao patent. During his deposition, however, Dr. Swanger conceded that the Xiao patent anticipated at least one of the claims in Terves’ patents. [Appx05704–05705.] As to infringement, Dr. Swanger analyzed multiple magnesium alloys that were brokered by Appellants. [Appx07013–07035.] He determined that some of the alloys infringed Terves’ ‘653 and ‘740 patents because there were nickel rich intermetallic phases in those alloys. [Appx07898–07899; Appx08698–08699.] Dr. Swanger opined that the intermetallic phase should be Mn_2Ni (2:1 ratio of magnesium to nickel), but the alloys from Appellants that he analyzed had less than 5% nickel. [*Id.*]

Appellants retained Dr. Dana Medlin. Dr. Medlin authored a 196-page report that challenged both validity and infringement with respect to all of the claims at issue. [Appx08788–08984.] Regarding validity, Dr. Medlin opined in his expert report and testified during deposition that all of the claims in Terves’ ‘653 and ‘740

patents were anticipated by the Xiao patent or obvious in view of Xiao combined with other references. [Appx08790 (“I conclude that the ‘653 and ‘740 are either anticipated by Xiao and/or obvious over combination of Xiao and Hassan; anticipated by Fripp ‘035; or made obvious.”).] When opining on validity—as is common when analyzing patent claims—Dr. Medlin grouped the claims from Terves’ patents. Even though he did not explicitly analyze each individual claim, he ultimately opined that all of the claims were anticipated or obvious. [Appx08790.] Regarding infringement, Dr. Medlin pointed out many problems with the data that Dr. Swanger relied upon, including the mis-scaled nature of the graphs Dr. Swanger used to purportedly show the presence of an intermetallic phase. [Appx09689–09693.] In his rebuttal report, Dr. Medlin produced correctly-scaled graphs to show that there was not a 2:1 ratio of magnesium to nickel in Appellants’ alloys, so the alloys did not infringe Terves’ patents. [Appx09691.]

II. Procedural History

Terves filed suit for patent infringement against Appellants⁵ on July 15, 2022 in the United States District Court for the Northern District of Ohio. Terves also moved for a preliminary injunction against Appellants [Appx00222], which the District Court denied. [Appx04177.] On August 7, 2020, Appellants filed a

⁵ Terves also filed suit against Yueyang Aerospace New Materials Co. Ltd., but that party was never served, and the District Court dismissed all claims against Yueyang on April 22, 2022. The dismissal of Yueyang is not at issue in this appeal.

Counterclaim against Terves seeking declaratory relief that Terves’ ‘010, ‘653, and ‘740 patents were invalid and/or unenforceable against Appellants.

Appellants moved for summary judgment on all of Terves’ claims on November 18, 2021. [Appx04428, Appx04431.] Terves also moved for summary judgment on its affirmative infringement claims and Ecometal and Nick Yuan’s affirmative defenses and counterclaim. [Appx06477, Appx07884.]

On April 12, 2022, the District Court entered an order denying in part and granting in part Appellants’ motion for summary judgment and also denying in part and granting in part Terves’ motion for summary judgment. [Appx00001–00019.] Specifically, with respect to Appellants’ motion, the Court found that “[m]aterial questions of fact remain as to whether any claims within the ‘653 and ‘740 Patents are invalid on the basis of anticipation or obviousness.” [Appx00018.] With respect to Terves’ motion, the District Court found as a matter of law that the accused Ecometal products infringed certain claims of the ‘653 and ‘740 Patents. The District Court further ruled that, for some of the claims of infringement, “Defendants have failed to provide sufficient evidence to support their defenses to the claims of infringement.”⁶ [*Id.*] For other claims of infringement on the ‘653 and ‘740 Patents, however, the District Court held that “material questions of fact remain as to whether

⁶ This one quote illustrates how the District Court got the analysis wrong. The burden is not on Appellants to come forward with evidence regarding infringement.

these claims are invalid on the basis of anticipation or obviousness.” [Appx00019.] Notably, the Court found that there were material factual issues regarding all independent claims. [*Id.*]

Following the District Court’s summary judgment order, Terves voluntarily withdrew the claims for which the District Court found material questions of fact on the issues of anticipation and obviousness. [Appx11469–11470.] Thus, the only issues remaining for trial were (1) whether Ecometal and Nick Yuan willfully infringed Terves’ patents and (2) damages. [Appx11472–11474.] Before, during, and after trial, Appellants’ Counsel argued that Nick Yuan could not be held personally liable for Ecometal’s infringement. The District Court rejected these arguments at every step and included Nick Yuan, personally, on the verdict form. [Appx11650–11652.] Ultimately, the jury found that the infringement was *not* willful, and awarded Terves \$707,207.00 in lost profit damages, less than half of what Terves requested at trial. [Appx00020–00022.]

Terves moved for a permanent injunction against Appellants on May 10, 2022. [Appx12530–12652.] Terves asked the District Court to enjoin Appellants and anyone acting in concert with them, including MMP, from importing or selling any infringing material. [*Id.*] Appellants opposed that motion, arguing that the required *e-Bay Inc.* four-factor test was not satisfied and that the District Court could not enter an order against non-party MMP. [Appx12754–12777.] The District Court

ultimately granted Terves’ motion on July 20, 2022, and entered a permanent injunction against Ecometal and Nick Yuan. [Appx00023–00030.] The District Court found that it was inappropriate to enter an injunction against MMP for any independent infringement. [Appx00029–00030.]

On May 26, 2022, Appellants filed a notice of appeal of the District Court summary judgment order and its inclusion of Nick Yuan on the verdict forms. Appellants subsequently filed a notice of appeal of the permanent injunction order on August 15, 2022, and the two appeals have been consolidated in the Federal Circuit. [App. Dkt 14.]

SUMMARY OF THE ARGUMENT

I. The District Court Erred in Granting Summary Judgment for Terves

The District Court should have permitted the jury to determine whether the Terves patents were invalidated by prior art and whether Appellants infringed on the Terves patents. Instead, the District Court ignored disputed facts to find infringement. Then, the District Court inexplicably and improperly distinguished between “challenged” and “unchallenged” infringement claims, finding validity was a jury question for the independent parent claims but that Appellants somehow “conceded” validity on the claims dependent on those independent parent claims. The District Court’s conclusion had no basis in law or fact. Not only does such a

holding fail logically, but the record evidence confirms that Appellants, in fact, challenged the validity of each and every one of Terves' claims.

As evidenced in Appellants' summary judgment briefing, Appellants challenged the validity of all of the claims in Terves' '653 and '740 patents. All of the claims were anticipated by and/or obvious under the Xiao patent—which was published *years before* Terves applied for its patents. Appellants' expert, Dr. Dana Medlin, submitted a 196-page report on this issue, and Terves' expert conceded invalidity during his deposition. The District Court erred in granting Terves' Motion for Summary Judgment instead of granting Appellants' Motion on this issue. This Court should reverse the District Court's decision on invalidity and hold as a matter of law that Terves' '653 and '740 patents are invalid. If this Court finds that Terves' patents are invalid, then the remaining issues on appeal do not need addressed.

Alternatively, and in addition, the District Court erred in finding that there was no disputed fact regarding infringement. Terves had the burden to prove Appellants' alloys infringed, and the evidence Terves submitted to the District Court—particularly its expert's analysis—failed to prove infringement. Further, Appellants' own expert submitted clear evidence showing noninfringement. The evidence submitted creates an issue of material fact regarding infringement, so the District Court erred in granting Terves' Motion for Summary Judgment on this issue. This Court should reverse the District Court's grant of summary judgment on the

issue of infringement and remand this case back to the District Court for a jury trial on infringement.

II. The District Court Erred in Permitting Nick Yuan to be Personally Liable

No matter the outcome of the summary judgment appeal, this Court should reverse the District Court's orders holding Nick Yuan personally liable and render judgment in his favor. It is well-established that, absent piercing the corporate veil, a court cannot hold an officer of a company liable for the infringement of the company. Even though Nick Yuan is the sole owner and employee of Ecometal, Nick Yuan cannot be held personally liable unless there was a showing that Nick Yuan acted outside the interests of Ecometal. Terves elicited *no* evidence during discovery, nor at trial, to show that Nick Yuan somehow acted outside the interests of Ecometal. And the District Court performed no analysis of Nick Yuan's personal liability for Ecometal's alleged infringement. On this record, Nick Yuan cannot be held personally liable for Ecometal's infringement.

III. The District Court Erred in Granting a Permanent Injunction

If the Court reverses or remands the District Court's summary judgment orders for any reason, then it must also reverse the District Court's entry of a permanent injunction against Appellants. But even if the final judgment in this case was correct (it is not), entry of a permanent injunction was still inappropriate. A permanent injunction is a drastic and extraordinary remedy that should be entered

only when no appropriate legal remedy exists. Terves did not come close to satisfying the 4-factor test under *e-Bay*: (1) Terves did not suffer an irreparable injury; (2) adequate remedies at law exist (*i.e.*, Terves was already awarded monetary damages); (3) an equitable remedy is not warranted; and (4) the public has no interest in this permanent injunction.

Further, the District Court’s permanent injunction order was improperly overbroad because it applied to non-party MMP. MMP was not a party to the lawsuit in the trial court, and it is well-established that permanent injunctions may not be entered against non-parties. This Court should reverse the District Court’s permanent injunction order.

ARGUMENT

I. The District Court Reversibly Erred In Granting Summary Judgment For Terves.

The District Court’s summary judgment ruling was wrong in two major ways. *First*, the District Court improperly found that Appellants did not “challenge” the validity – on the basis of anticipation or obviousness—of a subset of dependent claims within the ‘653 and ‘740 patents. And, *second*, the District Court improperly found that Appellants did not “sufficiently rebut” Terves’ evidence of infringement. Both errors require reversal.

A. Standard of Review

“This court reviews without deference a District Court’s grant of summary judgment and draws all justifiable inferences in favor of the nonmovant.” *Genentech, Inc. v. Amgen, Inc.*, 289 F.3d 761, 767 (Fed. Cir. 2002) (citing *Anderson v. Liberty Lobby, Inc.*, 477 U.S. 242, 255 (1986)). “In reviewing summary judgment rulings on infringement and invalidity, this court ‘need[s] to determine de novo whether the evidence in the record raises any genuine disputes about material facts.’” *Motionless Keyboard Co. v. Microsoft Corp.*, 486 F.3d 1376, 1379 (Fed. Cir. 2007) (quoting *General Elec. Co. v. Nintendo Co., Ltd.*, 179 F.3d 1350, 1353 (Fed. Cir. 1999)).

To defeat summary judgment, the nonmoving party need only provide evidence sufficient to establish a genuine issue of material fact regarding validity. *Freedman Seating Co. v. American Seating Co.*, 420 F.3d 1350, 1363 (Fed. Cir. 2005) (district court erred by holding that summary judgment for patent holder was appropriate because defendant had failed to prove invalidity by clear and convincing evidence; since “it was [plaintiff] who moved for summary judgment[,] ... [defendant] only needed to show the existence of a genuine issue of material fact in order to preclude summary judgment for [plaintiff]”).

Lastly, summary judgment on the issue of patent claim infringement is proper “when no reasonable jury could find that every limitation recited in the properly

construed claim either is or is not found in the accused device either literally or under the doctrine of equivalents.” *Gart v. Logitech, Inc.*, 254 F.3d 1334, 1339 (Fed. Cir. 2001). Determining whether a patent claim has been infringed is a two-step process: (1) claim construction to determine the scope of the claims, followed by (2) determination whether the properly construed claim encompasses the accused structure. *Id.* This Court’s review of the first step, claim construction, is *de novo*. *Id.*; *see also Bai v. L & L Wings, Inc.*, 160 F.3d 1350, 1353 (Fed. Cir. 1998). This Court’s review of the second step, determination of infringement, whether literal or under the doctrine of equivalents, is a question of fact subject to an abuse of discretion review. *Bai*, 160 F.3d at 1353; *North Am. Vaccine, Inc. v. Am. Cyanamid Co.*, 7 F.3d 1571, 1574 (Fed. Cir. 1993).

B. The District Court Incorrectly Ruled that Appellants Did Not “Challenge” Validity of Certain Claims

i. The District Court’s ruling that certain dependent claims were not “challenged” is contrary to Federal Circuit law.

Terves asserted infringement of both independent parent claims *and* dependent claims of the ‘653 and ‘740 Patents. In its summary judgment ruling, the District Court *correctly* found that “material questions of fact remain” as to whether the independent claims are invalid on the basis of anticipation or obviousness. [Appx00018–00019.] But the District Court inexplicably concluded that Appellants did not “challenge” the validity on the basis of anticipation or obviousness of the

claims that were dependent on those parent claims of those same patents. [Appx00018.] On its face, this was reversible error under Federal Circuit law.

The District Court provided no rationale as to why dependent claims are valid as a matter of law while the validity of the independent parent claim was an issue of fact for trial. “When a dependent claim and the independent claim it incorporates are not separately argued, precedent guides that absent some effort at distinction, the claims rise or fall together.” *Soverain Software LLC v. Newegg Inc.*, 728 F.3d 1332, 1335 (Fed. Cir. 2013) (emphasis added); *accord Speedfit, LLC v. Chapco, Inc.*, 490 F. Supp. 3d 575, n.9 (E.D.N.Y. 2020) (“the Court only examines the independent claim, and the validity of the dependent claims rises and falls with that of the independent claim”).

‘653 Claims	
Independent Parent Claims “Challenged”	Dependent Claims “Unchallenged” without distinction
1	2, 3, 9
12	14, 15, 18, 19, 20, 23
25	26, 27
29	30, 31
33	34, 35
37	38, 39
41	42
45	46, 47
49	50, 52 – 54, 56 – 61, 61, 64, 66, 67, 76
‘740 Claims	
2	3 – 5, 8-11, 13, 16, 17
19	20 – 47, 51 – 69, 76 – 93
94	95 – 103

[Appx00034–00083.]⁷

Terves never separately argued or distinguished between the independent parent and dependent claims, and the District Court never identified any such distinctions. Under this Court’s precedent, if the independent claims were held to be challenged, so too were the dependent claims deemed challenged unless Terves or the District Court explained why they are distinct. Since the Court found material factual disputes in connection with all the independent claims, it should have consequently found all the dependent claims to be challenged as well. For this reason alone, the District Court’s summary judgment decision should be reversed and, at a minimum, remanded for trial as to all claims.

ii. The District Court ignored admissible evidence challenging validity of all claims – independent and dependent.

The District Court erred in finding that Appellants did not dispute certain claims (all of which were dependent claims), labeling them as “unchallenged claims.” [Appx06496–06497, Appx08472–08473.] Specifically, in its summary judgment opinion, the District Court held: “[Appellants] do not dispute that Dr.

⁷ The District Court also held that some of the dependent claims were challenged. [Appx00014 (“Terves concedes that the Ecometal Defendants have offered some expert evidence creating a material question of fact on these defenses with regard to the remaining asserted claims.”); *see also* Appx11469 (in joint stipulation, Terves agreed that claims 1, 4, 5, 7, 12, 13, 25, 29, 33, 37, 41, 43, 45, 49, 55, 69-70, and 74 of the ‘653 patent and claims 2, 19, and 94 of the ‘740 patent were challenged by Appellants).] Appellants agree with the District Court that these claims were challenged and that a material issue of fact exists regarding validity of these claims.

Medlin has provided no opinion on anticipation or obviousness with regard to the unchallenged claims, and [Appellants] have not offered testimony from any competent non-expert POSITA on these issues.” [Appx00014.] The District Court then defined “unchallenged claims” as claims 2, 3, 9, 14, 15, 18-20, 23, 26, 27, 30, 31, 34, 35, 38, 39, 42, 46-47, 50, 52-54, 56-61, 64, 66, 67, and 76 of the ‘653 Patent and claims 3-5, 8-11, 13, 16, 17, 20-47, 51-69, 76-93, and 95-103 of the ‘740 Patent. [Id.] This was reversible error.

To arrive at this conclusion, the District Court ignored admissible expert testimony submitted by Appellants opining on the invalidity of these claims. Specifically, Appellants’ patent validity challenge started with the earlier-filed Xiao patent. Dr. Medlin testified that there were a set of “*several basic claim limitations*”—building blocks—that were repeated within Terves’ asserted claims and reorganized in myriad ways. [Appx08790 (emphasis added).] But, since each of the building blocks was obvious, it was obvious to reorganize them in the manner claimed in Terves’ patents. [Id.]

On summary judgment, the District Court was required to consider the admissible evidence in a light most favorable to the nonmoving party. *Tolan v. Cotton*, 572 U.S. 650 (2014). In *Tolan*, the Supreme Court vacated the Fifth Circuit’s affirmance of the grant of summary judgment where the District Court impermissibly “credited the evidence of the party seeking summary judgment and

failed properly to acknowledge key evidence offered by the party opposing that motion.” *Id.* at 657. If the District Court fails to consider all the relevant admissible evidence in favor of the non-movant, including expert testimony, its award of summary judgment should be reversed. *See Jacobs v. N.C. Admin. Off. of the Courts*, 780 F.3d 562, 570 (3rd Cir. 2015) (reversing summary judgment where the “District Court omits any mention of Dr. Coleman’s conflicting report” and concluding that the “court incorrectly drew all inferences in favor of the AOC, not Jacobs”).

The same result should occur here. The District Court never considered Dr. Medlin’s building block analysis for challenging the common elements of all of Terves’ claims. The District Court’s summary judgment ruling in favor of Terves should be reversed for this reason, too.

iii. The record evidence showed that Terves’ patents were anticipated by or obvious under the Xiao Patent.

Appellants presented evidence at summary judgment that all claims in Terves’ patents were either anticipated by the Xiao patent or obvious in view of the Xiao patent when combined with one or more references. [Appx08790 (“the ‘653 and ‘740 are either anticipated by Xiao and/or obvious” over Xiao combined with other references”).]

A patent is invalid for anticipation “if a single prior art reference discloses each and every limitation of the claimed invention.” *Schering Corp. v. Geneva Pharms.*, 339 F.3d 1373, 1377 (Fed. Cir. 2003) (citing *Lewmar Marine, Inc. v.*

Barient, Inc., 827 F.2d 744, 747 (Fed. Cir. 1987)). Moreover, “a prior art reference may anticipate without disclosing a feature of the claimed invention if that missing characteristic is necessarily present, or inherent, in the single anticipating reference.” *Id.* (citing *Continental Can Co. v. Monsanto Co.*, 948 F.2d 1264, 1268 (Fed. Cir. 1991)). Similarly, a patent is invalid “‘if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious’ to one of ordinary skill in the relevant art.” *Intercontinental Great Brands LLC v. Kellogg N. Am. Co.*, 869 F.3d 1336, 1343 (Fed. Cir. 2017) (quoting 35 U.S.C. § 103). Among the factual determinations are “the scope and content of the prior art, differences between the prior art and the claims at issue, the level of ordinary skill in the pertinent art, and any objective indicia of non-obviousness.” *Id.* (quoting *Randall Mfg. v. Rea*, 733 F.3d 1355, 1362 (Fed. Cir. 2013)).

Here, the District Court refused to conduct any analysis whatsoever into the Xiao patent. If the District Court had applied a proper analysis at summary judgment, it would have found that Terves’ patents were invalid as a matter of law or, alternatively, would have permitted Appellants to present this defense at trial. It is undisputed that the Xiao patent application was filed *years before* Terves filed its applications for the ‘653 or ‘740 patents. [*Compare* Appx12850 with Appx00034–000083.] If the Xiao patent anticipated the claims in Terves’ patents, then Terves’ patents are invalid.

Although the evidence submitted by Appellants was voluminous, the substantive analysis regarding anticipation and obviousness is quite simple: Terves used the basic principles from the Xiao patent and attempted to reorganize those principles to create a new patent. [Appx08790 (“each of the claims appears to be a reorganization of several basic claim limitations”).] But simply reorganizing or recombining a prior patent’s claims is not sufficient to create a new valid patent. Appellants will not rehash the entirety of their summary judgment briefing—which the District Court largely ignored (*see supra* at I.B.i)—but the most important evidence is summarized below. Based on a review of this evidence, it is clear the District Court erred in granting Terves motion for summary judgment and denying Appellants’ motion for summary judgment on the issues of anticipation and obviousness.

1. Appellants submitted expert testimony that each of the claims in Terves’ patents was merely a reorganization of the Xiao patent.

Appellants’ expert, Dr. Medlin, opined in his expert report that Terves’ patents were a restatement and reorganization of the Xiao patent:

...As detailed below, I conclude that the ’653 and ’740 are either anticipated by Xiao and/or obvious over the combination of Xiao...[and other specified references]....

With respect to the ‘653 and ‘740 Asserted Claims,⁸ and as I discuss further in the following paragraphs, *each of the claims appears to be a reorganization of several basic claim limitations*....¹⁰ In each of the ‘653 Asserted Claims, the magnesium [alloy] composite comprises: (A) magnesium (Mg) or a magnesium alloy; and (B) an “additive material” or “secondary metal.”

[Appx08789–08791.] Dr. Medlin discussed the “basic claim limitations”—the building blocks of the claims—in detail. Each building block was, in Dr. Medlin’s opinion, disclosed in prior art, primarily in the Xiao patent. This was not a bare assertion of fact by Dr. Medlin. He backed it up with a 196-page report to which were attached dozens of exhibits. [Appx08788–08983.]⁹

Dr. Medlin opined that all of the claims included specific basic building blocks. [Appx08791–08793.] Specifically, Dr. Medlin testified to the basic elements of 1) magnesium or a magnesium alloy, and 2) an additive material or secondary material. [Appx08791.] Next, in ¶ 11 Dr. Medlin notes in greater detail what the weight percentage ranges of each component was claimed. [Appx08791.] In ¶ 12 Dr. Medlin brings these points together in discussing why all of the “‘653 Asserted Claims are obvious over the combination of Xiao in view of Hassan.” [Appx08793.]

⁸ Dr. Medlin defined “Asserted Claims” to be all claims asserted by Terves in the litigation, so that his opinions clearly covered all relevant claims. [Appx08788–08789.]

⁹ The District Court did not criticize Dr. Medlin’s credentials or analysis.

For example, Claim 2 of Terves’ ‘653 patent depends on Claim 1 and adds specific additional additive materials selected from aluminum, boron, bismuth, zinc, zirconium, and manganese. [Appx00034–00053.] Claim 2 did not alter the fundamentals of Claim 1. [*Id.*] It added some fine detail regarding additional elements that could be used. [*Id.*] Dr. Medlin addressed all of those additional metals early in his report as some of the basic building blocks. [Appx08792.] Dr. Medlin also addressed that all of those elements were present in the prior art. [Appx08832–08835.] The metals added by Claim 2 were not earthshattering: they were minor additional implementations of a “substantially materially identical” invention. However, the District Court did not address the issues in that level of detail. Instead, the District Court incorrectly determined that Appellants did not “challenge” validity of a subset of claims. [Appx00014.]

Terves may argue that Dr. Medlin did not expressly discuss every single claim individually when providing invalidity opinions. [Appx06496–06497, Appx08472–08473.] While it is true that Dr. Medlin did not literally list out every single claim, his expert report and testimony nonetheless provided invalidity opinions as to each and every claim in Terves’ patents. [Appx08788–08983.] Specifically, Dr. Medlin’s analysis grouped various Terves’ claims together based on their common features. This analysis is not uncommon in cases where patent validity is challenged. *See, e.g., Hyatt v. Dudas*, 551 F.3d 1307, 1314 (Fed. Cir. 2008) (discussing a USPTO rule

allowing claims to be grouped and analyzed based on an exemplary claim selected from the group); *Dayco Prods., Inc. v. Total Containment, Inc.*, 329 F.3d 1358, 1370 (Fed. Cir. 2003) (“To be sure, it is permissible to group claims together for disposition where resolution involves the same issues of validity; however, the justification for such grouping is possible only where those issues are substantially materially identical.”); *CANVS Corp. V. United States*, 116 Fed. Cl. 294, 302 (Fed. Cl. 2014) (“Claims 6 and 7 will stand or fall together as two sides of the same coin”).

The District Court did not expressly reject Dr. Medlin’s building blocks analysis, nor did the District Court find that the claims Dr. Medlin “grouped” were not “substantially materially identical” to the claims that he challenged. But as explained in greater detail above, the District Court refused to conduct any substantive analysis whatsoever. *See supra* at I.B.¹⁰ This was clear reversible error.

2. Terves’ own expert conceded that Xiao anticipates claims in Terves’ patents.

Ultimately, *all* of the claims at issue in Terves’ patents include the phrase “*magnesium alloy*” without limiting that phrase in any manner. Notably, Terves’ expert, Dr. Lee Swanger, conceded that the claim term “magnesium alloy” is indefinite because the number of such alloys is infinite. [Appx05700.]

¹⁰ Notably, Appellants submitted substantially the same expert report and evidence in their *ex parte* proceeding, and the USPTO properly understood Appellants to have challenged all claims, and it accepted the evidence and rejected all claims in its first office action.

Specifically, Dr. Swanger, admitted that the elements disclosed in the Xiao patent are found in Claim 1 of Terves' '653 patent. During his deposition, Dr. Swanger conceded that *“it appears that [] example 4 from the Xiao patent is practicing Claim 1 of the ‘653 patent.”* [Appx05704–05705 (emphasis added).] Dr. Swanger attempted to backtrack from this admission, testifying that the claims of the '653 Patent might be distinguishable from the teachings of the Xiao patent because of the possibility that the copper and nickel might form an “alloy, which is not a precipitant.” [Appx05719.] However, Dr. Swanger later conceded in his deposition that an “alloy formed from cooling liquid” is a precipitant. [Appx05721.] By conceding that an alloy is a precipitant, Dr. Swanger's sole attempted distinction between Terves' '653 patent and the Xiao patent evaporated. This testimony effectively conceded that the Xiao patent anticipated all of Terves' '653 patent claims.

3. A jury or court could have found anticipation or obviousness even without expert testimony.

In reality, an expert is not even necessary to see that the '653 and '740 patents are anticipated by a plain reading of those patents in light of the Xiao patent. All of the claims in Terves' '653 and '740 patents uses the term “magnesium alloy.” But this term is not defined, and the plain reading of that term means a mixture of magnesium and any other metal. [Appx00034–00083.] So, any metallic element

combined with magnesium found in the Xiao patent would anticipate *all* magnesium alloys listed in ‘653 and ‘740 Patents.

For example, Claim 1 of Terves’ ‘653 patent recites:

[S]aid additive material having [1] a greater melting point temperature than a solidus temperature of said magnesium, [2] said additive material constituting about 0.05 wt. % - 45 wt. % of said mixture, [3] said additive material forming precipitant in said magnesium composite, [4] said additive material includes one or more metals selected from the group consisting of copper, nickel, iron, and cobalt, [5] said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

[Appx00049–00050.] Magnesium has a relatively low solidus temperature (melting point) of approximately 1202 °F. The other components cited by the Xiao patent except Zn have higher melting points as shown in the below table.

Metal	Melting Temperature (°F)
Zn	787
Mg	1,202
Al	1,221
Ag	1,763
Cu	1,984
Ni	2,651
Fe	2,800
Ti	3,034
Zr	3,371

The Xiao patent teaches the element of “additive material having a greater melting point than a solidus temperature of said magnesium,” as set forth in Claim 1. Therefore, this claim is anticipated by Xiao.

The Xiao patent also recites copper (Cu), nickel (Ni), iron (Fe), aluminum (Al), Zinc (Zn), silver (Ag), zirconium (Zr), titanium (Ti) within the specified concentration ranges. [Appx12852–12853.] A reference with a single chemical composition anticipates a claim covering multiple compositions. *Ecolochem, Inc. v. S. California Edison Co.*, 863 F. Supp. 1165, 1179 (C.D. Cal. 1994), *aff'd in part, rev'd in part*, 91 F.3d 169 (Fed. Cir. 1996). Therefore, the Xiao patent anticipates the “additive materials.”¹¹ Similarly, the Xiao patent shows dissolution rates in g/cm²/hr,¹² but the Xiao patent teaches magnesium mixtures above the 5 mg/cm²/hr required in Claim 1. Therefore, all of the limitations of Claim 1 of the ‘653 Patent are taught by the Xiao patent.

Claim 12 of the ‘653 patent provides another example. Claim 12 requires:

[A] magnesium composite comprising a mixture of a magnesium or a magnesium alloy and an additive material, said additive material having a greater melting point temperature than a solidus temperature of said magnesium, said composite including greater than 50 wt. % magnesium, said additive material constituting about 0.05-45 wt. % of said magnesium composite, said additive material having a melting point temperature that is 100° C greater than a melting temperature of said magnesium or magnesium alloy, said additive material including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium, and iron, at least a portion of said additive material remaining unalloyed additive material, said magnesium composite including in situ precipitation

¹¹ As noted above, Terves’ expert conceded that the additives described in the Xiao patent comprised a “precipitant” as the parties agreed to define that term.

¹² To convert to mg/cm²/hr the values in paragraph [0064] would be multiplied by a 1000 (or the decimal point moved to the right three numerals).

of galvanically-active intermetallic phases that includes said unalloyed additive material, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

[Appx00050.] All of these limitations are taught by the Xiao patent including the “magnesium alloy.” The Xiao patent teaches “additive materials” with “a melting point temperature that is 100 °C greater than a melting temperature of said magnesium or magnesium alloy.” Of course, since “magnesium alloy” is indefinite, the melting point of the magnesium alloy in Terves’ claims cannot be determined for a comparison.

Claim 25 in the ‘653 patent provides yet another example. This claim requires a:

[M]agnesium alloy composite comprising at least 85 wt. % magnesium; one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt.% zinc, 0.01-3 wt.% zirconium, and 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

[Appx00051.] Again, the Xiao patent teaches a composite that is exactly this mixture with the required properties. [*Compare* Appx00051 with Appx12850–12851.] Indeed, a detailed element-by-element comparison for each claim of the ‘653 and ‘740 patents is provided in Appellants’ Final Invalidity and

Noninfringement Contentions. [Appx05723–06047.] For this reason, too, the District Court erred in granting summary judgment as to validity on Terves’ claims and denying Appellants summary judgment motion as to invalidity.

C. Whether Appellants’ Alloys Infringed Terves’ Patents Is An Issue Of Fact.

The District Court erred in holding that Appellants infringed Terves’ patents as a matter of law. To prove infringement of a patent, “a patentee must supply sufficient evidence to prove that the accused product or process meets every element or limitation of a claim.” *Rohm & Haas Co. v. Brotech Corp.*, 127 F.3d 1089, 1092 (Fed. Cir. 1997); *see also Lemelson v. United States*, 752 F.2d 1538, 1551, 224 USPQ 526, 533 (Fed.Cir.1985) (“It is ... well settled that each element of a claim is material and essential, and that in order for a court to find infringement, the plaintiff must show the presence of every element ... in the accused device.”); *Laitram Corp. v. Rexnord, Inc.*, 939 F.2d 1533, 1535, 19 USPQ2d 1367, 1369 (Fed.Cir.1991) (“[T]he failure to meet a single limitation is sufficient to negate infringement of the claim....”). As the patent owner, Terves bears the burden to prove that Appellants infringed. *Medtronic, Inc. v. Mirowski Family Ventures, LLC*, 571 U.S. 191, 198, 199 (2014).

The record evidence demonstrated unresolved disputed issues of fact with respect to at least one key requirement of each of the claims in Terves’ patents: the presence of an “intermetallic phase” in Appellants’ allegedly infringing alloys.

Indeed, it is undisputed that one requirement of all the claims in Terves' patents is the presence of an "intermetallic phase," also called an "*in situ* precipitate." [Appx00049–00050; Appx00080; *see also* Appx00009 (court noting in summary judgment opinion that infringement revolved around whether Terves proved that a "galvanically active intermetallic phase[]" existed in Appellants' alloys).] The alloys described in Terves' patents have first a magnesium phase and a second phase containing a higher percentage of one or more additive materials. [Appx00049–00050; Appx00080.] The second phase is the "intermetallic" or "*in situ* precipitate."

Relevant intermetallics have a fixed stoichiometry—a ratio—between the metals comprising the intermetallic. Terves' expert, Dr. Swanger, admitted that within relevant temperatures and compositions, the ratios of metals cannot be changed for a specific combination of magnesium with a secondary metal, such as nickel or copper; the intermetallic will always be 2:1 and the secondary metal cannot be less. [Appx08702 (Terves' expert opining that for Appellants' alloys, given the relevant conditions, "the only intermetallic phases that will form are either Mg_2Cu or Mg_2Ni ").] Ultimately, the evidence Terves submitted to the District Court was disputed as to whether Appellants' alloys were at the required 2:1 ratio, or so-called "copper-rich" or "nickel-rich." This means that summary judgment on infringement was improper.

i. Terves' expert analysis failed to prove the required nickel-rich intermetallic phases in Appellants' alloys.

Terves' expert, Dr. Swanger, examined Appellants' alloys and reviewed the ratios within the magnesium phase and the purported intermetallic phase. [Appx07898–07899; Appx08698–08699.] To prove infringement, the intermetallic phase should have included 1/3 nickel. But the graphs and data produced by Terves' expert showed that the amount of nickel in the magnesium phase was about the same as the amount of nickel in the purported intermetallic phase. Neither the magnesium phase nor the purported “intermetallic” were nickel rich.

The rebuttal report of Appellants' expert further demonstrated Terves' failure to establish the existence of a nickel-rich intermetallic phase and, thus, disputed Terves' claims of infringement. [Appx08782–08784.] Appellants' expert opined, for example, that:

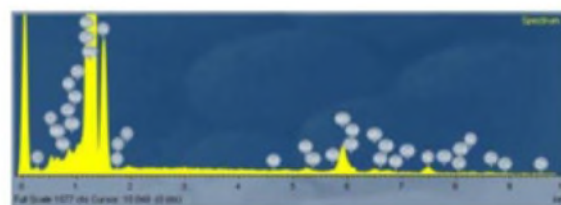
The EDS scans presented in the Swanger report show a huge Mg peak. In fact, you cannot see the top of the Mg peak because it extends beyond the top of the EDS scan. ***When comparing the very large Mg peak to the very small Ni and Cu peaks, the 33% ratio is not even close to being met. Dr. Swanger's opinion that the EDS scans in his analysis prove these areas in the samples are Mg₂Ni and Mg₂Cu intermetallic phases is incorrect.*** These areas do have slightly higher amounts of Ni and Cu when compared to the matrix areas, but clearly the Ni and Cu peak intensities are far too low to conclude that these areas are Mg₂Ni and Mg₂Cu intermetallic phases.

[Appx08782–08783 (emphasis added).] And Appellants explicitly disputed Terves' purported “undisputed” Facts 13 and Fact 15. [Appx08637–08638.]

The District Court erred by not even recognizing, let alone mentioning, these disputed facts. Instead, the District Court accepted Terves' unsupported argument that Appellants' expert did not offer any non-infringement opinions. [*Compare* Appx09895–09897 *with* Appx00010 (finding that “Dr. Medlin, has offered no non-infringement opinion.”).] Dr. Medlin did, in fact, offer several non-infringement opinions [Appx09689–09693] and, in any event, Terves had the burden to affirmatively establish infringement as a matter of law at the summary judgment stage. The data from Terves' own expert showed otherwise.

ii. Late-produced analytical data from Terves further negated the existence of purported “intermetallic phases” required to show infringement.

At the eleventh hour, Terves submitted a report from its expert, Dr. Swanger, that included mis-scaled graphs purporting to show that Appellants' alloys contained the required 2:1 ratio of Magnesium-Nickel (Mg_2Ni) or Magnesium-Copper (Mg_2Cu). [Appx08698–08699.] Appellants reproduced that graph in their Response to Terves' Motion for Summary Judgment, and included with it a properly scaled graph using the exact same data:



Swanger Jul 27, 2021 Rep. at 15 (Spectrum 1)

Figure 2

[*Id.* p. 15 (Swanger's disproportional graph).]

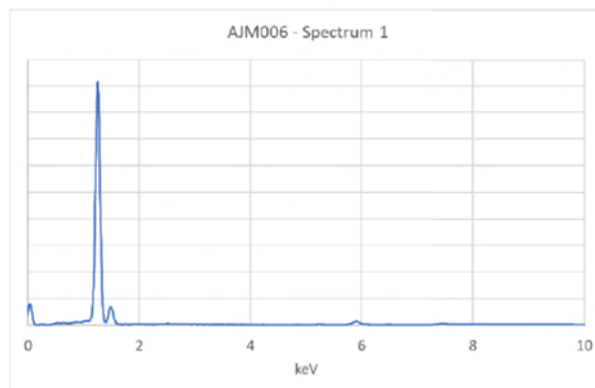


Figure 3

[Appx09691 (correctly scaled version of graph).]

As shown, the larger the peak, the higher the concentration of that element is present. Conversely, an element with low concentration would present as a small peak, and an element not present would show no response at all. Terves misleadingly attempted to use Dr. Swanger's graph to prove that the first large magnesium peak is approximately 2 times the size of the second copper/nickel peak. But, as Appellants showed, viewing a correctly scaled graph shows that the second copper/nickel peak is, in fact, less than 2% of the magnesium. This 2% is far less than the required 2:1 ratio under Terves' patents. And without the presence of Mg_2Ni or Mg_2Cu , there is no infringement.

Terves did not argue that Appellants' graphs inaccurately represented Dr. Swanger's experimental results. [Appx09896–09897.] Rather, Terves complained

only that the “data” was “unauthenticated.”¹³ [*Id.*] The District Court erred in accepting this argument, finding that the display of *data provided by Terves own expert* was “attorney argument and unauthenticated graphs.” [Appx00009.]

Setting aside that the underlying data displayed in Appellants’ brief was provided by Terves’ own expert, Federal Rule of Evidence 1006 allows this type of summary evidence to be admitted at trial. Specifically, FRE 1006 provides that the “proponent may use a summary, *chart*, or calculation to prove the content of voluminous writings, recordings ... that cannot be conveniently examined in court.” (Emphasis added.) Further, the question regarding admitting summaries is generally accuracy. *United States v. Anekwu*, 695 F.3d 967, 982 (9th Cir. 2012), *cert. denied*, 569 U.S. 989 (2013); *United States v. Blackwell*, 436 Fed. Appx 192, 199 (4th Cir. 2011), *cert. denied*, 565 U.S. 1160 (2012) (“appellants do not suggest that they were deprived of the opportunity to examine the underlying records or challenge the accuracy of the summary in court”).

The District Court completely rejected the simple summary of data provided by Terves’ own expert that showed, at a minimum, a disputed issue of fact with respect to infringement. In fact, the graphical summaries contained admissible

¹³ Terves also argued that these graphs should have been submitted by Appellants’ expert, Dr. Medlin. But it was impossible for Appellants’ expert to include this data in his report, because the data was provided late by Terves’ own expert after Appellants’ expert already submitted his report.

evidence¹⁴ showing that intermetallic particles were not present in Appellants' alloys. That means summary judgment on infringement was improper.

II. The District Court Erred In Holding Nick Yuan Personally Liable.

A. Standard of Review

The Federal Circuit reviews a District Court's decision on a motion for judgment as a matter of law, as well as asserted errors in jury instructions, under the law of the regional circuit. *Syngenta Crop Protection, LLC v. Willowood, LLC*, 944 F.3d 1344, 1355 (Fed. Cir. 2019); *Barry v. Medtronic, Inc.*, 914 F.3d 1310, 1332 (Fed. Cir. 2019). The Sixth Circuit reviews a denial of a motion for directed verdict de novo. *Estate of Riddle ex rel. Riddle v. Southern Farm Bureau Life Ins. Co.*, 421 F.3d 400, 407-408 (6th Cir. 2005). Similarly, the Sixth Circuit "reviews jury instructions to determine whether they are a correct interpretation of the relevant law." *Gibson v. City of Louisville*, 336 F.3d 511, 512 (6th Cir. 2003). "Because the

¹⁴ Moreover, the District Court erred in concluding this summary evidence would not have been admissible at trial. FRCP 56, 2010 Advisory Committee Notes on subdivision (c)(2). The Advisory Committee notes that the process "functions much as an objection at trial, adjusted for the pretrial setting." *Id.* Ultimate admissibility need not be determined but rather only whether the evidence is "capable of being admissible at trial." *FOP v. City of Camden*, 842 F.3d 231, 238 (3rd Cir. 2016); *Humphreys & Partners Architects, L.P. v. Lessard Design, Inc.*, 790 F.3d 532, 538 (4th Cir. 2015) ("court may consider...the content or substance of otherwise inadmissible materials where the 'the party submitting the evidence show[s] that it will be possible to put the information... into an admissible form'").

correctness of jury instructions is a question of law, they are reviewed de novo.” *Id.*, citing *Jones v. Federated Fin. Reserve Corp.*, 144 F.3d 961, 966 (6th Cir. 1998).

B. There is no Evidence to Support Nick Yuan’s Personal Liability.

The District Court erred in finding that Nick Yuan could be held personally liable for the alleged infringement by Ecometal. It is well-established that, absent piercing the corporate veil, a court cannot hold an officer of a company liable for the infringement of the company unless there is evidence of “bad faith, fraud, or culpable intent.” *Hoover Grp., Inc. v. Custom Metalcraft, Inc.*, 84 F.3d 1408, 1412 (Fed. Cir. 1996) (reversing District Court’s imposition of personal liability where there was no evidence that the corporate officer engaged in bad faith or had fraudulent intent, noting, “unless the corporate structure is a sham, . . . personal liability for inducement to infringe is not automatic but must be supported by personal culpability”).

In other words, you cannot punish a one-person company if that person was acting in the interests of the company. *Banyan Licensing, L.C. v. OrthoSupport Int’l, Inc.*, 296 F. Supp. 2d 885, 892 (N.D. Ohio 2003). In *Banyan Licensing*, the court explained that to hold a corporate officer personally liable, the plaintiff must establish that the officer “maintained an interest separate from that of [the company]”—i.e., that the officer’s conduct diverted from the scope of his office. *Id.* The court ultimately granted the corporate officer’s motion for summary judgment where the officer’s “conduct never exceeded the practical, business and financial

interests of [the company].” *Id.* The court also noted, “Because [the company] is essentially a one-person corporation, [the officer] was necessarily heavily involved in every facet of its activities. [Plaintiff] should not be able to take advantage of this circumstance alone to hold [the officer] personally liable.” *Id.*

Under the standards set forth in *Hoover* and *Banyan Licensing*, Nick Yuan should not be held personally liable for any infringement by Ecometal. Even though Nick Yuan is the sole owner and employee of Ecometal, Nick Yuan cannot be held personally liable unless there is a showing that Nick Yuan acted outside the interests of Ecometal. Terves elicited *no* evidence during discovery, nor at trial, to show that Nick Yuan somehow acted outside the interests of Ecometal. Absent this evidence, Nick Yuan cannot, as a matter of law, be held personally liable for Ecometal’s infringement.

During trial, Appellants moved the District Court on two separate occasions to dismiss Nick Yuan from the case. First, Appellants moved for a directed verdict. [Appx12327–12328 (“[T]he defense moves for directed verdict on the remaining claims left in the trial. . . . The first part is seeking dismissal of Mr. Yuan individually.”).] The District Court denied that motion. [Appx12349.] Second, Appellants moved to remove Nick Yuan, individually, from the jury instructions and verdict forms. [Appx11590.] The District Court also rejected Appellants’ proposed

jury instructions and included Nick Yuan on the verdict forms. [Appx11650–11652 (including “Defendants” on the verdict forms instead of just Ecometal).]

Accordingly, even if Ecometal was found to infringe a valid patent of Terves, the District Court erred in denying Nick Yuan’s motion for a directed verdict on this issue and then including Nick Yuan in the jury instructions and on the jury verdict forms.

III. The District Court Erred in Entering a Permanent Injunction.

A. Standard of Review

“The decision to grant or deny permanent injunctive relief is an act of equitable discretion by the District Court, reviewable on appeal for abuse of discretion.” *eBay Inc. v. MercExchange, L.L.C.*, 547 U.S. 388, 391 (2006). The Court “may find an abuse of discretion on a showing that the court made a clear error of judgment in weighing relevant factors or exercised its discretion based upon an error of law or clearly erroneous factual findings.” *Apple Inc. v. Samsung Elecs. Co., Ltd.*, 735 F.3d 1352, 1359 (Fed. Cir. 2013).

B. Even if Appellants Infringed Valid Patents, Entry of a Permanent Injunction Was Still Inappropriate.

The Patent Act provides that in cases of patent infringement a District Court “*may* grant injunctions in accordance with the principles of equity.” 35 U.S.C. § 283 (emphasis added). A plaintiff seeking a permanent injunction must demonstrate (1) that it has suffered an irreparable injury; (2) that remedies available at law, such as

monetary damages, are inadequate to compensate for that injury; (3) that, considering the balance of hardships between the plaintiff and defendant, a remedy in equity is warranted; and (4) that the public interest would not be disserved by a permanent injunction. *eBay*, 547 U.S. at 391. Per the *eBay* Court, these “familiar principles apply with equal force to disputes arising under the Patent Act.” *Id.*

In applying these principles, the Court should consider that an “injunction is a drastic and extraordinary remedy, which should not be granted as a matter of course.” *Monsanto Co. v. Geerston Seed Farms*, 561 U.S. 139, 165 (2010). For this reason, the Supreme Court has cautioned that an “injunction should issue only where the intervention of a court of equity ‘is essential in order effectually to protect property rights against injuries otherwise irremediable.’” *Weinberger v. Romero-Barcelo*, 456 U.S. 305, 312 (1982) (quoting *Cavanaugh v. Looney*, 248 U.S. 453, 456 (1919)). Hence, “[i]f a less drastic remedy ... [is] sufficient to redress [a plaintiff’s] injury, no recourse to the additional and extraordinary relief of an injunction [is] warranted.” *Monsanto*, 561 U.S. at 165–66.

As Terves’ patents are neither valid nor were infringed, a permanent injunction should never have been entered. Regardless, even if this Court determines that the District Court correctly held that Appellants infringed Terves’ valid patents, there was no basis for the District Court to enter a permanent injunction against

Appellants and non-party MMP, as Terves did not satisfy the 4-factor *eBay* test. Accordingly, the permanent injunction should be vacated.

1. The District Court Reversibly Erred In Finding That Terves Was Likely To Suffer From Irreparable Harm For Which There Did Not Exist An Adequate Legal Remedy

The District Court erred when it held that Terves was likely to suffer from irreparable harm for which there is no adequate legal remedy if a permanent injunction was not entered against Appellants and MMP, for *three* primary reasons.¹⁵

First, the District Court erred in concluding that Appellants and Terves are direct competitors and therefore a permanent injunction was warranted. [Appx00024.] The record is clear that Terves and Appellants do not directly compete with one another with respect to the sale of fracking balls and plugs, which is the primary source of Terves' sales and therefore the principal basis of its assertion that it is suffering "harm." [Appx12540–12541.] Appellants only broker sales of dissolvable magnesium billets; they do not sell fracking balls and plugs made up of the dissolvable cast magnesium, as Terves does. In concluding that Appellants and Terves were direct competitors and therefore Terves was likely to suffer irreparable harm, the District Court improperly conflated Appellants with non-party MMP,

¹⁵ The district court considered the first two factors of the permanent injunction analysis, irreparable harm and inadequate legal remedy, together. [Appx00024.] Because the first two factors are so closely related, this Court has often analyzed them together. *See, e.g., ActiveVideo Networks, Inc. v. Verizon Commc'ns, Inc.*, 694 F.3d 1312, 1337 (Fed. Cir. 2012). Appellants do so here.

which is Appellants' former customer for their dissolvable magnesium billets, and which does directly compete with Terves in the fracking ball and plug market. [Appx00025.] Because Terves and Appellants are not direct competitors, there is no direct loss of market share due to Appellants' infringement.

This Court's decision in *ActiveVideo Networks, supra*, is analogous to the instant case. There, the District Court granted a permanent injunction to the patentee, ActiveVideo, against the infringer, Verizon, which incorporated the infringing features in its FIOS-TV product. This Court reversed the injunction, holding that a monetary award would be sufficient to compensate ActiveVideo for its injury. The Court emphasized that ActiveVideo and Verizon were not competitors: ActiveVideo sold hardware and software to providers of video services, while Verizon sold video services to end users. It was ActiveVideo's customer, Cablevision, that directly competed with Verizon and was at risk of losing end-use customers to Verizon due to Verizon's infringement. Hence, the Court concluded that because the District Court's finding of irreparable harm "was based in large part on the loss of market share to Cablevision" it was "clearly erroneous." *Id.* at 1338.

Here, Terves and Appellants do not directly compete in the fracking ball and plug marketplace. The District Court's finding of irreparable harm was largely based

on Terves’ alleged loss of market share to Appellants’ customer, MMP. As this Court held in *ActiveVideo*, this finding constitutes reversible error.¹⁶

Second, the District Court erred when it determined that a reasonable royalty was not an available adequate legal remedy. The District Court did not even analyze whether a reasonable royalty was appropriate under the circumstances; it simply concluded that absent any desire by Terves to negotiate a licensing agreement, the District Court would not “force the parties into a licensing agreement.” [Appx00026.] This was clear error.

In cases where the parties fail to come to an agreement regarding a licensing agreement, the District Court is empowered to impose an ongoing royalty *sua sponte* upon the parties. *See Paice LLC v. Toyota Motor Corp.*, 504 F.3d 1293, 1315 (Fed. Cir. 2007) (noting that “[s]hould the parties fail to come to an agreement, the District

¹⁶ Even if non-party MMP’s direct competition with Terves was relevant to the question of whether a permanent injunction should have been entered against Appellants, a permanent injunction would still be inappropriate under these facts. Courts are more likely to award injunctive relief when the direct competitors are the only players in the relevant market. *See Humanscale Corp. v. CompX Intern. Inc.*, No. 3:09–CV–86, 2010 WL 1779963, at *3 (E.D. Va. Apr. 29, 2010) (denying motion for permanent injunction and reasoning that the “direct competition typically used to justify a finding of irreparable harm involves a two competitor market, which is not the case here”). Undisputed trial evidence shows that in 2018, Halliburton, Innovex, Baker Hughes, and Schlumberger supplied 72.5% of the market share of dissolvable magnesium fracking balls and plugs. [Appx12849.] Neither Terves nor MMP are among these top suppliers of dissolvable magnesium fracking balls and plugs.

Court could step in to assess a reasonable royalty in light of the ongoing infringement”); *Telcordia Technologies, Inc. v. Cisco Systems, Inc.*, 612 F.3d 1365, 1379 (Fed. Cir. 2010) (stating that if the “parties cannot reach an agreement [on a reasonable royalty], the District Court should step in and assist or calculate on its own the appropriate rate”).

Following the *eBay* decision and its rejection of presumed injunctive relief, courts are increasingly more likely to award future running royalties instead of injunctions. *ActiveVideo Networks, supra*, is on point once more. There, the court reversed a grant of permanent injunction and remanded the case to the District Court to determine a reasonable ongoing royalty rate for future infringement by the defendant, Verizon. *Id.* at 1341. The court reasoned that the harm to ActiveVideo due to Verizon’s infringement was “readily quantifiable” and ActiveVideo could be fully compensated for the ongoing infringement by Verizon’s payment of a royalty for each end-use customer who used ActiveVideo’s invention. *Id.* at 1338.

Terves has an adequate remedy at law—a reasonable running royalty that could be assessed to the infringing dissolvable magnesium billets sold by Appellants. And while the District Court was persuaded that it should not impose a reasonable royalty where Terves had refused to enter into a licensing agreement with Appellant, the District Court failed to consider that Terves had repeatedly argued that reasonable royalty damages were relevant for trial and that the jury should be

instructed on that type of damages. [Appx12335–12337 (opposing Appellants’ motion for directed verdict on the reasonable royalty issue).] This directly cuts against any argument that Terves’ harm would be difficult to measure. Because Terves’ harm can be adequately redressed via monetary damages in the form of a reasonable royalty, the District Court abused its discretion in failing to impose such a royalty.

Third, the District Court erred when it rejected Appellants’ argument that demand for Terves’ frac balls and plugs is not tied to the intrinsic value of the patented dissolvable cast magnesium. As Appellants argued to the District Court, sales lost to an infringing product cannot irreparably harm a patentee if consumers buy that product for reasons other than the patented feature. The demand “must be tied to the intrinsic value of the patented feature.” *See Calico Brand, Inc. v. Ameritek Imps., Inc.*, 527 F. App’x. 987, 996 (Fed. Cir. 2013). Thus, a likelihood of irreparable harm cannot be shown if sales would be lost regardless of the infringing conduct. *See Apple, Inc. v. Samsung Elecs. Co., Ltd.*, 678 F.3d 1314, 1324 (Fed. Cir. 2012). Particularly relevant here, “where damages are based on sales of a multicomponent product that includes both infringing and non-accused components, in the absence of an apportionment, a patentee must prove that the patented features are the primary driver of demand for the entire product.” *Good Tech. Corp. v. MobileIron, Inc.*, No. 5:12-CV-05826-PSG, 2015 WL 3882608, at *4 (N.D. Cal June 23, 2015). It is “not

enough to merely show that the patented feature is viewed as valuable, important or even essential to the use of the entire accused product,” but rather, the more essential inquiry is “whether the plaintiff can show that each or any of the patented features creates the basis for customer demand.” *Id.* (quoting *LaserDynamics, Inc., v. Quanta Computers, Inc.*, 694 F.3d 51, 67–68 (Fed. Cir. 2012) (internal quotations omitted)).

The evidence presented at trial showed that the design of the fracking plugs—as opposed to the patented dissolvable magnesium—drove sales for the product. [Appx11911–11912 (Terves’ corporate representative agreed that there is a specific design for the fracking plugs and that each of his customers have their own design); Appx11974 (another Terves employee acknowledges that the fracking plug admitted into evidence as Exhibit 3 was a KLX design); Appx11975–11976 (Doud explained that some designs are “simpler” and “easier to manufacture” than others, and that there are specific “design considerations” that go into developing fracking plugs).] This testimony demonstrates that the design of a fracking plug is important to customers. Terves did not establish at trial that the patented feature—i.e., the dissolvable magnesium formulation—drove demand for the product as opposed to the specific design of the fracking plug. The District Court should have found that there was no irreparable injury for this reason alone.

The District Court rejected this argument because Appellants “focuse[] solely an [sic] alleged value in the specific design of fracking plug sold not by Ecometal,

but by MMP.” [Appx00026.] But this misses the point. Terves itself argued that the irreparable harm it suffered due to Appellants’ infringement was the sales of frac plugs and balls it lost to MMP, focusing particularly on lost sales of frac tools from its customer KLX. [Appx12540–12541.] As the evidence at trial demonstrated that the product design, and not the patented dissolvable magnesium, was the primary driver of demand for the frac tools, Terves failed to satisfy its burden of proving irreparable harm. The District Court erred in holding otherwise.

2. The District Court Erred In Holding That The Balance Of Hardships Weighs In Favor Of An Injunction

The District Court also erred in holding that the third factor, balance of hardships, weighed in favor of injunctive relief. [Appx00027–00028.] The balance of hardships factor “assesses the relative effect of granting or denying an injunction on the parties.” *i4i Ltd. P’ship v. Microsoft Corp.*, 598 F.3d 831, 862 (Fed. Cir. 2010).

Appellants presented evidence that a permanent injunction would be a significant detriment to Nick Yuan personally as the sole proprietor and lone employee of Ecometal, and that as a small business owner Yuan even had difficulty paying the legal fees needed to defend himself in the case. [Appx11819, Appx12034–12035, Appx12119–12120.] Appellants also presented evidence that Appellants’ business depends on Yuan maintaining relationships with companies in

the metal industry, and that entry of a permanent injunction would seriously harm Appellants' reputation in the industry. [Appx12831–12833.]

The District Court concluded that the balance of hardships favored an injunction because there was “testimony at trial that the loss of sales and customers attributable to the availability of the infringing product caused hardship to Terves and its employees.” [Appx00027.] But the evidence at trial showed that these hardships were largely attributable to the Covid-19 pandemic, not Appellants' infringing conduct. The District Court ignored that Terves' own damages expert conceded many of these layoffs occurred due to the Covid-19 pandemic, and that Terves' own sales numbers from 2021 show that its sales have risen substantially since the Covid-19 pandemic subsided. [Appx12204; Appx12847–12848.]

On balance, Appellants are more negatively impacted by the District Court's entry of a permanent injunction than Terves would be in the absence of injunctive relief. This is especially true because Terves' harm can be remedied via monetary damages. The District Court abused its discretion in holding that the balance of hardships favored entry of the drastic remedy of a permanent injunction.

3. The District Court Erred In Holding That The Public Interest Would Not Be Disserved By Entry Of An Injunction

Lastly, the District Court erred in concluding that the public interest would not be disserved by entry of a permanent injunction against Appellants. The District Court gave this final factor mere lip service, and instead of conducting a genuine

analysis relied upon the truism that the general public has an interest in the enforcement of patent laws. [Appx00028.] This was insufficient. “Although enforcing the right to exclude serves the public interest, the public interest factor requires consideration of other aspects of the public interest.” *ActiveVideo, supra*, at 1341; *see also* Donald A. Chisum, Chisum on Patents § 20.04[2][c][vii] (2009) (“The proper question on the public interest should be: will an injunction harm a specific public interest that outweighs the public’s interest in a robust patent system?”) (internal citations and quotation marks omitted).

The Eastern District of Texas’s decision in *z4 Techs., Inc. v. Microsoft Corp.*, 434 F. Supp. 2d 437 (E.D. Tex. 2006) is apposite. There, the court found that the public interest was likely to be disserved if a permanent injunction was entered against Microsoft enjoining it from utilizing certain software technology that z4 Techs patented. Microsoft asserted that “a redesign of its products could result in the products being taken off the market for a short period of time.” *Id.* at 443. The court agreed, finding that “there is a risk that certain sectors of the public might suffer some negative effects.” *Id.* at 444. The court also noted that it was “unaware of any negative effects that might befall the public in the absence of an injunction.” *Id.*

As Appellants argued to the District Court, like in *z4 Techs*, here, the public could also “suffer some negative effects” from a permanent injunction. Due to recent global events and the current U.S. economy, oil and gas companies are searching for

new sources of oil, particularly local sources within the United States. Both the oil and gas companies and individual consumers could suffer additional negative effects if the District Court's overbroad permanent injunction is permitted to stand. The District Court's failure to consider these countervailing factors constituted reversible error.

C. The Permanent Injunction is Overbroad as to MMP.

Even if the Court affirms the District Court's entry of a permanent injunction against Appellants, it should still reverse the District Court's order precluding MMP from purchasing any "infringing materials." MMP was not a party to the lawsuit in the District Court, and it is well-established that permanent injunctions may not be entered against non-parties. *See Additive Controls & Measurement Sys., Inc. v. Flowdata, Inc.*, 96 F.3d 1390, 1397 (Fed. Cir. 1996) (reversing District Court's entry of permanent injunction against non-party).

In *Additive Controls*, after judgment was entered following a bench trial, which found that the patent at issue was valid and the defendants infringed, the plaintiff moved for a permanent injunction. *Id.* at 1392. The initial proposed order was directed only to the defendant and "its officers, agents, servants, employees, attorneys, and those persons in active concert or participation with them who receive actual notice of this Final Judgment." *Id.* However, the order was later revised to explicitly name a non-party. *Id.* (explaining that the District Court noted the entities

were not parties to the underlying action, but “found that each of the [non-parties] had received notice of the original injunction and ruled that the injunction was therefore binding on them”). Following entry of the injunction order, the non-parties filed motions under Federal Rule of Civil Procedure 60(b) seeking relief. *Id.* The District Court denied their request for relief and the non-parties appealed to the Federal Circuit. *Id.* at 1393.

On appeal, the Federal Circuit agreed with the non-parties that the permanent injunction order entered against them was improper. The Federal Circuit first explained that the general language regarding “persons in active concert or participation” allows a non-party to be held in contempt only for “assisting the enjoined party in violating the injunction.” *Id.* at 1395. A non-party cannot be held in contempt or be subject to sanctions for “engaging in ***independent conduct*** with respect to the subject matter of th[e] [underlying] suit.” *Id.* (emphasis added). The Federal Circuit also rejected the plaintiff’s argument that the All Writs Act authorized the District Court to “issue commands” to non-parties “as may be necessary or appropriate to effectuate and prevent the frustration of orders it has previously issued.” *Id.* at 1396. The Federal Circuit found the All Writs Act did not apply and specifically explained,

Although an injunctive order prohibiting non-parties from [infringing] may be more efficient than a separate lawsuit against those parties, the All Writs Act does not authorize that kind of adjudicative shortcut. With regard to their independent activities (i.e., activities independent

of [Defendants]), the corporate appellants are entitled to contest their liability and the appropriateness of equitable relief in a lawsuit in which they are named as parties.

The order directing the appellants not to [infringe] is in effect an open-ended injunction against the sale of those [infringing products] directed to entities that have not had an opportunity to contest [plaintiff's] assertion that those [products] infringe a valid patent. It is true that the District Court has made a determination that the '318 patent is valid (in the [underlying lawsuit]) and that the [products at issue] infringe that patent . . . But . . . those rulings do not apply to entities such as the appellants, which have not had an opportunity to litigate those issues in a case in which they were named as parties. **If [the plaintiff] wishes to obtain permanent injunctive relief against the appellants based on their independent activities, it cannot do so by seeking an injunction against them in a case to which they are not parties; it must, instead, validly serve them and obtain an adjudication of infringement against them.**

Id. at 1397 (emphasis added). The Federal Circuit went on to re-emphasize that its opinion in this case “stems from the basic principle that an injunction ordinarily cannot be imposed on a non-party that has not had the opportunity to contest its liability.” *Id.* at 1397.

In its Opinion granting Terves’ motion for permanent injunction, the District Court agreed with Appellants that “[i]t would not be appropriate . . . to enjoin MMP from any independent conduct, whether or not that conduct is alleged to constitute infringement.” [Appx00029.] The District Court acknowledged that as a non-party, MMP “has not had an opportunity to address” the arguments made by Terves, and it had not been proven that MMP’s final fracking products infringed Terves’ patents. [*Id.*] Nonetheless, in its formal Order, the District Court permanently enjoined MMP

“from purchasing any Infringing Materials, or any material covered by the Infringed Claims.” [Appx00023–00024.] In other words, this order precludes MMP from selling “any material” that could be covered by Terves’ patents. Under *Additive Controls*, the trial court’s permanent injunction order is overbroad, as Terves has not presented any evidence that MMP’s final products infringe Terves’ patents, and MMP has not an opportunity to defend itself in this case. If Terves wanted to impose a permanent injunction on MMP, it should have “validly served [it] and obtain[ed] an adjudication of infringement against [it].” *Additive Controls*, 96 F.3d at 1397. The District Court clearly erred by entering an order that applied to non-party MMP.

CONCLUSION

The District Court’s orders on summary judgment, Nick Yuan’s personal liability, and injunctive relief were all improper. For all of the reasons stated above, Appellants respectfully request that this Court reverse and remand the District Court’s summary judgment order and subsequent judgment. Specifically, Appellants request that this Court:

- (1) Reverse the District Court’s summary judgment decision on invalidity and infringement because there are material issues of fact, and remand this case for a jury trial on these issues or, alternatively, find invalidity as a matter of law.
- (2) Reverse the District Court’s denial of Appellants’ motion for directed verdict on Nick Yuan’s personal liability because, as a matter of law,

Nick Yuan cannot be held personally liable for any alleged infringement by Ecometal.

- (3) Reverse the District Court's entry of a Permanent Injunction against Appellants because Terves did not satisfy the *e-Bay* 4-factor test, and because the District Court did not have jurisdiction to enter a permanent injunction against non-party MMP.

Dated: December 8, 2022

s/Martin S. High

*COUNSEL FOR DEFENDANTS-
APPELLANTS*

ADDENDUM

IN THE UNITED STATES DISTRICT COURT
FOR THE NORTHERN DISTRICT OF OHIO
EASTERN DIVISION

TERVERS, LLC,)
)
 Plaintiff.)
)
 v.)
)
 YUEYANG AEROSPACE NEW)
 MATERIALS CO. LTD., *et al.*,)
)
 Defendants.)
)
)

CASE NO.: 1:19 CV 1611

 JUDGE DONALD C. NUGENT

MEMORANDUM OPINION
AND ORDER

This matter is before the Court on Plaintiff's Motion for Summary Judgment (ECF #135, 136), and Defendants' Amended Motion For Summary Judgment. (ECF #134, 137). Each party filed a response in opposition to the opposing party's motion, and a reply in further support of their own. (ECF #143, 144, 147, 148). Following the allowance of supplementary discovery, Defendants filed a Supplement to their Motion for Summary Judgment, and Plaintiff filed a Response. (ECF #151, 153). On March 29, 2022, the USPTO issued a Notice of Intent to Issue *Ex Parte* Reexamination Certificate, and Plaintiff filed a Notice re *Ex parte* Reexamination Confirming Patentability, along with arguments as to how it might affect Defendants defenses and

counterclaims. (ECF #174). Defendants then filed a Response to Terves' Notice. (ECF #177).

Plaintiff also filed a Motion to Strike the January 10, 2022 Declaration of Dr. Dana Medlin, which had been filed in support of the Defendants' Reply in support of its motion for summary judgment. (ECF #150). Defendants filed an opposition to this motion, and Plaintiff filed a reply in support. (ECF #152, 153). Finally, Plaintiff filed a Motion to Bifurcate Inequitable Conduct, which Defendants opposed. (ECF #169, 176). After careful consideration of the briefs and a thorough review of all relevant evidence and authority, the Court finds as follows.

FACTS AND PROCEDURAL HISTORY¹

Terves LLC, ("Terves") is a developer and manufacturer of engineered materials used in oil and gas drilling, and is the owner of asserted U.S. Patent No.10,329,653 ("the '653 Patent"), and U.S. Patent No. 10,689,740 ("the '740 Patent"). The '653 Patent, and the '740 Patent, address fully dissolvable magnesium materials used to manufacture frac balls and frac plugs. Ecometal is a Canadian company that sources metals and alloys. Nick Yuan is the CEO of Ecometal. Ecometal sells dissolvable magnesium to at least one client.

Terves filed suit against Yueyang Aerospace New Materials Co. Ltd. ("Yueyang"), Ecometal Inc. ("Ecometal"), and Nick Yuan alleging violations of two patents, U.S Patent No. 9,903,010 ("the '10 Patent") and U.S. Patent No. 10, 329, 653 ("the '653 Patent"). (ECF #1).

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The facts and procedural history have been taken from the undisputed statements set forth in the parties' briefs, and official court records. In accordance with the applicable standards on a motion for summary judgment, genuine questions of material fact have been resolved in favor of the non-moving party.

Defendants Ecometal and Nick Yuan (collectively “the Ecometal Defendants”) filed a Motion to Dismiss, and Terves, in response filed a First Amended Complaint. (ECF #13).² Terves subsequently filed a Second Amended Complaint, adding a claim for infringement of a third patent, U.S. Patent No. 10,689,740 (“the ‘740 Patent”). (ECF #44). The Ecometal Defendants Answered the Second Amended Complaint, asserting several affirmative defenses, along with three Counterclaims for Unenforceability, one for each of the three subject Patents (“the ‘10 Patent; the ‘653 Patent; and, the ‘740 Patent). (ECF #49). This Answer was later amended. (ECF #66). In response to the Ecometal Defendants’ Counterclaims, Terves filed a Motion to Dismiss, which was denied. (ECF #69, 85). During the claim construction process, Terves withdrew all claims under the ‘010 Patent. (ECF #45).

The Counterclaims allege that Terves engaged in inequitable conduct by failing to provide the United States Patent and Trademark Office with a complete English translation of the Xiao Patent when it submitted its Information Disclosure Statement identifying potentially relevant prior art in connection with its Patent Applications for the ‘010 and ‘653 Patents. The Ecometal Defendants also allege that Terves failed to provide any version of the Xiao Patent to the Patent Office during prosecution of the ‘740 Patent application, and that it failed to disclose the invalidity claims raised in this litigation during the ‘740 Patent prosecution.

During the course of this litigation, Ecometal initiated an *ex parte* reexamination of the ‘653 Patent by the USPTO. (ECF #100-1). In its arguments to the USPTO, Ecometal included a full English translation of the Xiao Patent. On November 19, 2021, the USPTO initially issued a “non-final rejection,” of the ‘653 Patent. On March 28, 2022, however, it issued a Notice of

²To date, Defendant Yueyang has not made an appearance in this case.

Intent to Issue *Ex Parte* Reexamination Certificate confirming all of the asserted claims in this litigation.³(ECF #174-1, PageID #15457).

STANDARD OF REVIEW

Summary judgment is appropriate when the court is satisfied “that there is no genuine issue as to any material fact and that the moving party is entitled to a judgment as a matter of law.” FED. R. CIV. P. 56(c). The burden of showing the absence of any such “genuine issue” rests with the moving party:

[A] party seeking summary judgment always bears the initial responsibility of informing the district court of the basis for its motion, and identifying those portions of ‘the pleadings, depositions, answers to interrogatories, and admissions on file, together with affidavits, if any,’ which it believes demonstrates the absence of a genuine issue of material fact.

Celotex Corp. v. Catrett, 477 U.S. 317, 323 (1986) (citing FED. R. CIV. P. 56(c)). A fact is “material” only if its resolution will affect the outcome of the lawsuit. *Anderson v. Liberty Lobby, Inc.*, 477 U.S. 242, 248 (1986). Determination of whether a factual issue is “genuine” requires consideration of the applicable evidentiary standards. The court will view the summary judgment motion in the light most favorable to the party opposing the motion. *Matsushita Elec. Indus. Co. v. Zenith Radio Corp.*, 475 U.S. 574, 587 (1986).

Summary judgment should be granted if a party who bears the burden of proof at trial does not establish an essential element of their case. *Tolton v. American Biodyne, Inc.*, 48 F.3d

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Claims 12-15,18-20, 23, 34, 67, and 69 were amended. (ECF #174-1, PageID #15457). Neither party has submitted any evidence that would suggest that the amended status of these claims in any way alters the arguments or issues pending in the current litigation.

937, 941 (6th Cir. 1995) (citing *Celotex*, 477 U.S. at 322). Accordingly, “[t]he mere existence of a scintilla of evidence in support of the plaintiff’s position will be insufficient; there must be evidence on which the jury could reasonably find for the plaintiff.” *Copeland v. Machulis*, 57 F.3d 476, 479 (6th Cir. 1995) (citing *Anderson*, 477 U.S. at 252). Moreover, if the evidence presented is “merely colorable” and not “significantly probative,” the court may decide the legal issue and grant summary judgment. *Anderson*, 477 U.S. at 249-50 (citations omitted). In most civil cases involving summary judgment, the court must decide “whether reasonable jurors could find by a preponderance of the evidence that the [non-moving party] is entitled to a verdict.” *Id.* at 252. However, if the non-moving party faces a heightened burden of proof, such as clear and convincing evidence, it must show that it can produce evidence which, if believed, will meet the higher standard. *Street v. J.C. Bradford & Co.*, 886 F.2d 1472, 1479 (6th Cir. 1989).

Once the moving party has satisfied its burden of proof, the burden then shifts to the non-mover. The non-moving party may not simply rely on its pleadings, but must “produce evidence that results in a conflict of material fact to be solved by a jury.” *Cox v. Kentucky Dep’t of Transp.*, 53 F.3d 146, 149 (6th Cir. 1995). FED. R. CIV. P. 56(e) states:

When a motion for summary judgment is made and supported as provided in this rule, an adverse party may not rest upon the mere allegations or denials of the adverse party’s pleading, but the adverse party’s response, by affidavits or as otherwise provided in this rule, must set forth specific facts showing that there is a genuine issue for trial.

The Federal Rules identify the penalty for the lack of such a response by the nonmoving party as an automatic grant of summary judgment, where otherwise appropriate. *Id.*

Though parties must produce evidence in support of and in opposition to a motion for summary judgment, not all types of evidence are permissible. The Sixth Circuit has concurred

with the Ninth Circuit's position that "only admissible evidence may be considered by the trial court in ruling on a motion for summary judgment." *Wiley v. United States*, 20 F.3d 222, 225-26 (6th Cir. 1994) (quoting *Beyene v. Coleman Sec. Servs., Inc.*, 854 F.2d 1179, 1181 (9th Cir. 1988)). FED. R. CIV. P. 56(e) also has certain, more specific requirements:

[Rule 56(e)] requires that affidavits used for summary judgment purposes be made on the basis of personal knowledge, set forth admissible evidence, and show that the affiant is competent to testify. Rule 56(e) further requires the party to attach sworn or certified copies to all documents referred to in the affidavit. Furthermore, hearsay evidence cannot be considered on a motion for summary judgment.

Wiley, 20 F.3d at 225-26 (citations omitted). However, evidence not meeting this standard may be considered by the district court unless the opposing party affirmatively raises the issue of the defect.

If a party fails to object before the district court to the affidavits or evidentiary materials submitted by the other party in support of its position on summary judgment, any objections to the district court's consideration of such materials are deemed to have been waived, and [the Sixth Circuit] will review such objections only to avoid a gross miscarriage of justice.

Id. at 226 (citations omitted).

As a general matter, the district judge considering a motion for summary judgment is to examine "[o]nly disputes over facts that might affect the outcome of the suit under governing law." *Anderson*, 477 U.S. at 248. The court will not consider non-material facts, nor will it weigh material evidence to determine the truth of the matter. *Id.* at 249. The judge's sole function is to determine whether there is a genuine factual issue for trial; this does not exist unless "there is sufficient evidence favoring the nonmoving party for a jury to return a verdict for that party." *Id.*

Summary judgment is as appropriate in a patent case as in any other type of case. *Desper*

Prods., Inc. V. QSound Labs, Inc., 157 F.3d 1324, 1332 (Fed. Cir. 1998). The defense of non-infringement may appropriately be decided on summary judgment if no reasonable jury could find that every limitation recited in a properly construed claim is found in the accused product either literally or under the doctrine of equivalents. *U.S. Philips Corp. v. Iwasaki Elec. Co. Ltd.*, 505 F.3d 1371, 1374 (Fed. Cir. 2007); *see also Lucent Technologies, Inc. v. Gateway, Inc.*, 525 F.3d 1200 (Fed. Cir. 2008). Both parties agree that there is undisputed evidence in this case generally establishing how the accused product works, and there are no genuine issues of material fact that would prevent a summary judgment ruling on the issue of infringement.

ANALYSIS

I. Infringement

Defendants seek summary judgment on infringement but offer no argument or evidence in favor of this request. Their Memorandum in Support of Defendants' Motion for Summary Judgment and their Reply brief focus solely on a variety of arguments relating to the validity of the patent but do not address infringement in any way. They have not even attempted to meet the criteria that would allow for summary judgment in their favor on the issue of infringement.

However, claims originally brought by Terves under the '010 Patent were subsequently withdrawn, and are, therefore, dismissed with prejudice. Plaintiff has also withdrawn claims 8, 11, 24, 28, 32, 36, 40, 44, 48, 51, 71, 72, and 75 of the '653 Patent, and claim 18 from the '740 Patent. Consequently, these claims are also dismissed with prejudice.

Plaintiff also seeks summary judgment on the issue of infringement. They seek an Order declaring that Ecometal's products, specifically AJM-006, AJM-010, AJM-012, AJM-016,

AJM017, AJM018, and AJM-023 (collectively “the AJM products” or “AJM composites”), infringe claims 1-5, 7, 9, 12-15, 18-20, 23, 25-27, 29-31, 33-35, 37-39, 41-43, 45-47, 49-50, 52-61, 64, 66-67, 69-70, 74, and 76 of the ‘653 Patent, and claims 2-5, 8-11, 13, 16-17, 19-47, 51-69, 76-103 of the ‘740 Patent. A patent is infringed when a person “without authority makes, uses, offers to sell or sells any patented invention, within the United States . . . during the term of the patent.” 35 U.S.C. § 271(a). “Literal infringement exists when every limitation recited in the claim is found in the accused device.” *Akzo Nobel Coatings, Inc. v. Dow Chem. Co.*, 811 F.3d 1334, 1341(Fed. Cir. 2016). Terves, as the accuser, bears the burden of proving, by a preponderance of the evidence, that Ecometal’s accused products infringe the patent(s).

The Ecometal Defendants do not dispute that they import, sell, and/or offer the accused AJM products for sale in the United States. Terves has offered the expert opinion of Dr. Swanger in support of its position that the AJM products infringe the above listed claims within the ‘653 and ‘740 Patents. Dr. Swanger tested the AJM products, through the use of chemical composition, corrosion, Scanning Electron Microscopy (“SEM”) and energy dispersive X-ray spectroscopy (“EDS”) testing. (ECF #136-9). Based on his testing he opined that the seven AJM products infringe the following claims: 1-5, 7, 9, 12-15, 18-20, 23, 25-27, 29-31, 33-35, 37-39, 41-43, 45-47, 49-50, 52-61, 64, 66-67, 69-70, 74, and 76 of the ‘653 Patent, and claims 2-5, 8-11, 13, 16-17, 19-47, 51-69, and 76-103 of the ‘740 Patent.

With regard to the ‘653 Patent, the Ecometal Defendants argue that the accused products do not contain an “additive material constituting about 0.05 st. %-45 st.% of a mixture that forms a “galvanically-active intermetallic,” as required for claims 1, 12, 25, 29, 33,37, 41, 45 and 49; and that there is no proof that unalloyed additive material remains as required for claim 12 and its

derivative claims 13-15, 18-20, and 23. Dr. Swanger's report concluded that all seven AJM products did contain a mixture that forms a galvanically-active intermetallic, and that the additive material was within the specified range. (ECF #144-2, PageID# 12530, 12570). The report also did identify "unalloyed additive material" in all seven grades of material in the accused products. (ECF #144-2, PageID# 12573). Ecometal has offered nothing more than attorney arguments and unauthenticated graphs to challenge Dr. Swanger's opinion that "galvanically active intermetallic phases" are present in the accused products. Neither of these constitute admissible evidence, and neither is sufficient to undermine the opinion of Plaintiff's expert. *See Vivid Technologies, Inc. v. Am. Science & Eng'g. Inc.*, 200 F.3d 795, 812 (Fed. Cir. 1999); *Impax Laboratories Inc. v. Lannett Holdings Inc.*, 893 F.3d 1372, 1380 (Fed. Cir. 2018).

With regard to the '740 Patent, the Ecometal Defendants argue that Terves has not shown the accused products are "frac balls, plugs, or other tool components." The Patent does not include a claim limitation requiring that the products take the form of "frac balls, plugs, or other tool components." This phrase appears in the preamble of the claim which describes "the use of an invention" and "generally do[es] not limit the claims." *Catalina Mktg. Int'l, Inc. v. Coolsavings.com, Inc.*, 289 F.3d 801, 809 (Fed. Cir. 2002). Further, the Ecometal Defendants did not raise this preamble language during the claim construction period, which would have been required under the Local Patent Rules. *See Id.*

The Ecometal Defendants also argue that there is no evidence that the AJM products contain *in situ* precipitates no more than 50 microns as required for claims 19 and its derivatives 20-47, 49-69, and 76-93; and, that there is no proof that the *in situ* precipitate includes additive

material.⁴ The Ecometal Defendants’ argument that the accused products have not been shown to fall within the size limitation is unsupported. Dr. Swanger’s infringement report specifically states that the “size of a plurality of the precipitates in each of the accused Ecometal composites is less than 50 microns, as shown by the micrographs in Exhibit D.” (ECF #144-2, PageID #12530, 12532). The photographs in exhibit D include a size scale that show that the precipitates are less than 50 micron. (ECF #144-2, PageID # 12548-12561). Further, after evaluating the accused composites and comparing them to the Patent claims, Dr. Swanger opined that the *in situ* precipitate includes additive material. (ECF #144-2, PageID #12589). The Ecometal Defendants offer no expert opinion or other evidence to contradict the evidence contained in Dr. Swanger’s report, or his related conclusions with regard to infringement.

Defendants’ expert, Dr. Medlin, has offered no non-infringement opinion. He testified that he began testing the accused composites to determine whether there was infringement but upon finding results that mirrored Dr. Swanger’s results he stopped testing. Although his report included one paragraph addressing infringement, within which he criticized Dr. Swanger’s testing, he offered no rebuttal to Dr. Swanger’s testing results or conclusions. He also admitted during his deposition that his report does not include an infringement analysis, or a non-infringement opinion, nor does it identify any accused AJM products that do not infringe the ‘653 or ‘740 Patents. (ECF #136-11, PageID 12234-12236). When a plaintiff meets its burden of

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Defendants argue that “Dr. Swanger’s EDS experiment purportedly shows *in situ* precipitate with no discernable additive materials.” (ECF #144, PageID #12476). They do not cite to any evidence in the record that supports this statement, nor do they concede the validity of the “purported” showing. There is no citation to any actual evidence that would provide a context within which this statement could be properly evaluated.

showing infringement and that showing goes effectively un-rebutted, summary judgment on infringement is appropriate. *See McGinley v. Franklin Sports, Inc.*, 262 F.3d 1339, 1344-49 (Fed. Cir. 2001)(affirming summary judgment when infringer's only rebuttal was conclusory).

Terves has submitted evidence sufficient to show that the accused AJM products infringe the above-listed claims of its '653 and '740 Patents, and Ecometal has not sufficiently rebutted any of this evidence. Therefore, assuming the patents are valid, Terves is entitled to summary judgment on its infringement claims. These claims may not be fully realized, however, if the Patents are found to be invalid or if any of the Defendants' other affirmative defenses apply. The asserted defenses will be addressed below.

II. Defenses

A. Patent-Ineligibility/Indefiniteness/Enablement/Written Description

Plaintiff has moved for summary judgment in its favor on the invalidity defenses of patent-ineligibility, indefiniteness, enablement, and written description. Patents are presumed valid. 35 U.S.C. § 282. An accused infringer must prove invalidity by clear and convincing evidence. *See Microsoft Corp. v. I4I Ltd. P'ship*, 564 U.S. 91, 131 S. Ct. 2238, 2239 (2011). Also, according to Local Patent Rules, a defendant must assert any grounds they have for invalidity in their final invalidity contentions. Defendants failed to assert 35 U.S.C. §101 as a grounds for invalidity in its final invalidity contentions, as is required under Local Patent Rule 3.5(d), 3.10. Further they have offered no expert opinion on their defenses of patent-ineligibility, non-enablement, or lack of written description. Each of these defenses is properly examined from the perspective of a person having ordinary skill in the art ("POSITA"), at the time the

patent was filed. *See, Nautilus, Inc. v. Biosig Instruments, Inc.*, 572 U.S. 898 (2014); *Apple Inc. v. Samsung Elecs. Co.*, 786 F.3d 983, 1002 (Fed. Cir. 2015), rev'd and remanded on other grounds, 137 S. Ct. 429 (2016). Therefore testimony from an expert or a non-expert POSITA is required to support these defenses. Conclusory assertions are insufficient. *See, Streck, Inc. v. Rsch. & Diagnostic Sys., Inc.*, 665 F.3d 1269, 1290 (Fed. Cir. 2012). Defendants have not provided any such testimony in support of these asserted defenses, and have not responded to the request for summary judgment on these defenses in their opposition.

With regard to indefiniteness, a patent claim is indefinite only if when “read in the light of the specification delineating the patent, and the prosecution history, [the claim] fail[s] to inform, with reasonable certainty, those skilled in the art about the scope of the invention.” *Nautilus, Inc. v. Biosig Instruments, Inc.*, 134 S. Ct. 2120, 2124, 189 L.Ed.2d 37 (2014). Ecometal has the burden of proving indefiniteness by clear and convincing evidence. *See BASF Corp. v. Johnson Matthey Inc.*, 875 F.3d 1360, 1365 (Fed. Cir. 2017). That burden has not been met. Dr. Medlin offered indefiniteness opinions in the claim construction report, but those opinions were rejected by the Court. (ECF #89). He indicated in his report that the patent does not specify a required method for testing dissolution rates, elongation, shear strength, and other limitations, but does not indicate why any generally acceptable method of testing would not suffice. (ECF #134-22). Nor does he opine that the rates and other limitations are not, themselves, properly definite and understandable to a POSITA. He criticizes the breadth of some limitations, but breadth is not the legal equivalent of indefiniteness. *See SmithKline Beecham Corp. v. Apotex Corp.*, 403 F.3d 1331, 1341 (Fed. Cir. 2005). This does not satisfy the burden of clear and convincing evidence of invalidity. Therefore, summary judgment in favor of Terves is appropriate, on these defenses.

See Shire LLC v. Amneal Pharms., LLC, 802 F.3d 1301, 1309 (Fed. Cir. 2015).

B. Waiver/Laches/Estoppel/Prosecution History Estoppel

Plaintiff moved for summary judgment on the defenses of waiver, laches, and estoppel. The Ecometal Defendants have not presented any evidence to support these asserted defenses, and have not responded to Plaintiffs request for summary judgment on these issues. Summary judgment in favor of Terves on these defenses is, therefore, appropriate.

C. Anticipation/Obviousness

Relevant to this issue is Defendants' attachment of a January 10, 2022 Declaration of Dr. Medlin, to their Reply in support of their motion for summary judgment and incorporated by reference in their opposition to Terves' Motion for Summary Judgment. (ECF#147-2).

Defendants cite the Declaration as support for their defenses of indefiniteness, anticipation, and obviousness. They assert that the declaration "clarifies" Dr. Medlin's prior expert report(s).

Terves filed a Motion to Strike this Declaration. The Court agrees that the Declaration should be stricken and will not consider it in connection with the summary judgment motions. The

Declaration, filed well after the close of expert discovery, expands and arguably contradicts opinions set forth in Dr. Medlin's expert reports and deposition. Further, the Declaration

indicates the Dr. Medlin "agrees" with the USPTO's non-final rejection of claims, referencing inadmissible evidence that has since been overturned. It would also be prejudicial to Terves to

have to address these new contentions after summary judgment briefing has been completed.

The Court finds that the Declaration is untimely, not harmless, and not substantially justified. *See HLV, LLC v. Van Buren County*, 775 Fed.Appx. 204, 214 (6th cir. 2019). Therefore, the motion to strike is GRANTED.

Terves seeks summary judgment on the Defendants' defenses of anticipation and obviousness, with regard to claims 2, 3, 9, 14, 15, 18-20, 23, 26, 27, 30, 31, 34, 35, 38, 39, 42, 46-47, 50, 52-54, 56-61, 64, 66, 67, and 76 of the '653 Patent; and claims 3-5, 8-11, 13, 16, 17, 20-47, 51-69, 76-93, and 95-103 of the '740 Patent (hereinafter, collectively "unchallenged claims").⁵ Terves concedes that the Ecometal Defendants have offered some expert evidence creating a material question of fact on these defenses with regard to the remaining asserted claims. The Ecometal Defendants do not dispute that Dr. Medlin has provided no opinion on anticipation or obviousness with regard to the unchallenged claims, and Defendants have not offered testimony from any competent non-expert POSITA on these issues. Summary judgment of no invalidity is appropriate when an accused infringer offers no expert, or other competent non-expert testimony that would provide evidence of invalidity from the perspective of a POSITA. *See Alexsam, Inc. v. IDT Corp.*, 715 F.3d 1336, 1348 (Fed. Cir. 2013); *Schumer v. Lab. Computer Sys., Inc.*, 308 F.3d 1304, 1315-16 (Fed. Cir. 2002). A laypersons's logic, judgment, and common sense, is not sufficient in a case, such as this, that involves complex scientific principles. Invalidity contentions are also not sufficient to supplant the required evidence on a motion for summary judgment. *See, generally Suffolk Technologies, LLC v. AOL Inc.*, 752 F.3d 1358, 1367 (Fed. Cir. 2014). Therefore, summary judgment is warranted, in favor of Terves, on the unchallenged claims.

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In its Memorandum in support of its Motion for Summary Judgment, Terves omits claims 26 and 53 of the '653 Patent from its list of unchallenged claims. (ECF #134-22). Terves also inadvertently included claim 94 in its list of unchallenged claims within the '740 Patent, although Dr. Medlin did address this claim in his expert report.

D. Inequitable Conduct

“Inequitable conduct is an equitable defense to patent infringement that, if proved, bars enforcement of a patent.” *Therasense, Inc. v. Becton, Dickinson & Co.*, 649 F.3d 1276, 1285 (Fed. Cir. 2011)(*en banc*). In order to prove inequitable conduct based on failure to disclose information, a defendant must show that the patent applicant (1) failed to disclose a known material reference; and (2) had a specific intent to deceive the USPTO. *Id.* at 1290. In order to properly present this defense, the pleadings must include sufficient allegations of underlying facts from which a court may infer that these two factors can be met. *Exergen Corp. v. Wal-Mart Stores, Inc.*, 575 F.3d 1312, 1328-29 (Fed. Cir. 2009). “Intent to deceive the Pto must be ‘the single most reasonable inference able to be drawn from the evidence.’” *Everlight Elecs. Co. v. Nichia Corp.*, 143 F.Supp. 3d 644, (E.D. Mich. 2015), *aff’d* 719 F.App’x 1008 (Fed. Cir. 2018). Materiality is proven by establishing that one or more claims within the patent would not have issued if the applicant had disclosed the withheld information. *Therasense* at 1291. Intent to deceive requires the defendant to show that the applicant “knew of the reference, knew it was material, and made a deliberate decision to withhold it.” *Id.* at 1290.

The Ecometal Defendants claim that Terves failed to disclose the full English translation of the Xiao prior art when it sought the ‘653 Patent, and that it failed to disclose that the patent was originally rejected by the Chinese Patent Office. It also claims that Terves withheld the existence of this litigation, as well as the English translation of Xiao obtained during this litigation, from the USPTO during the pendency of the ‘740 Patent prosecution. “[C]laims of inequitable conduct that are based on such omissions require proof of but-for materiality.” *Therasense*, 649 F.3d at 1293.

All of the allegedly withheld materials were submitted to the USPTO as part of the *ex parte* reexamination proceedings for the ‘653 Patent, initiated by Ecometal. On March 28, 2022, the USPTO issues a Notice of Intent to Issue *Ex Parte* Reexamination Certificate confirming the asserted claims. (ECF #174-1, PageID #15457). The Statement of Reasons for Patentability and/or Confirmation states that “Xiao is the closest prior art and it fails to teach a magnesium alloy that includes in situ galvanically-active intermetallic phases or intermetallic particles to enable controlled dissolution of the magnesium alloy as claimed.” The USPTO further noted that “[t]here is no suggestion from Xiao to substitute copper, nickel, iron or cobalt for the aluminum in the galvanically-active intermetallic.” (ECF #174-1, PageID #15458).⁶ The USPTO came to this conclusion having full knowledge of the English translation of the Xiao prior art reference; the office action initially denying Terves’ Chinese patent application; Terves’ response to the Chinese office action; notice of this litigation; the Court’s construction of terms in the ‘653 Patent; Defendants invalidity contentions; and, Dr. Medlin’s expert reports from this litigation. (ECF #174-2, PageID #15462-64). The examiner’s notes indicate that all of these documents were not only submitted, but considered by him during the reexamination process. (ECF #174-2, Page ID #15462-64).⁷ Because the USPTO confirmed patentability with full knowledge of all of

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The Ecometal Defendants argue that Plaintiff improperly inundated the USPTO with prior art references, however, there is no evidence that any of these references were actually improperly disclosed or unnecessary to a full review. Further, it is clear from the examiner’s statements that he was able to focus his analysis on the ‘653 Patent’s relationship to Xiao, which Defendants have consistently argued was the most relevant prior art.

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At the bottom of each list of references, the examiner initialed the following statement: “all references considered except where lined through /SV/.” None of the above cited references were lined through.

the materials Ecometal alleges were wrongfully withheld during the initial determination of patentability, those materials cannot be deemed to have been material. The materiality analysis is not affected by Defendants assertion that the USPTO's reasoning for confirming patentability was flawed. The question with regard to inequitable conduct is whether the patent holder withheld material information, not whether the USPTO's decision was ultimately correct. The fact that both the original and reexamination examiners made the same decision, one with and one without the information at issue, precludes a finding that the information was material. Absent clear and convincing evidence that Terves withheld material information, Defendants claim of inequitable conduct cannot be sustained.⁸

Although the USPTO reexamination only confirmed claims within the '653 Patent, there is no reason to believe that the allegedly withheld information would have any greater effect on the patentability of the '740 Patent. The Ecometal Defendants maintain the burden of proving the materiality of the information by clear and convincing evidence, and has presented no evidence that would suggest that the '740 Patent would not have been issued if the information allegedly withheld had been presented during that prosecution of that patent. Having failed to establish inequitable conduct by clear and convincing evidence, Ecometal's defense, as well as its second and third counterclaims, fail as a matter of law.

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Defendants argue that even if they cannot establish inequitable conduct, they could still prove invalidity based on the doctrine of unclean hands. However, Defendants did not assert the defense of unclean hands in their Amended Answer and Counterclaim, nor did they argue it in their Motion for Summary Judgment or their Response to Terves' Motion for Summary Judgment.

CONCLUSION

For the reasons set forth above, Defendants' Motion for Summary Judgment is GRANTED in part, and DENIED in part. (ECF #137). Claims originally brought by Terves under the '010 Patent are dismissed with prejudice. Claims 8, 11, 24, 28, 32, 36, 40, 44, 48, 51, 71, 72, and 75 of the '653 Patent, and claim 18 from the '740 Patent are also dismissed with prejudice. Material questions of fact remain as to whether any claims within the '653 and '740 Patents are invalid on the basis of anticipation or obviousness. Defendant has not provided sufficient evidence to prove their remaining defenses by the requisite standard of proof. Defendants' request for summary judgment on these issues is, therefore, DENIED.

Plaintiff's Motion for Summary Judgment is GRANTED in part and DENIED in part. (ECF #135, 136). The Defendants' defenses of waiver, laches, estoppel, and prosecution estoppel are not supported. The '653 and '740 Patents are not invalid due to patent-ineligible subject matter, non-enablement, indefiniteness, inequitable conduct, or lack of adequate written description. The Ecometal Defendants' counterclaims seeking declaratory judgment invalidating the '653 and '740 Patents due to inequitable conduct also necessarily fail along with the inequitable conduct defense.

The accused Ecometal products infringe claims 2, 3, 9, 14, 15, 18-20, 23, 26, 27, 30, 31, 34, 35, 38, 39, 42, 46, 47, 50, 52-54, 56-61, 64, 66, 67, and 76 of the '653 Patent, and claims 3-5, 8-11, 13, 16, 17, 20-47, 51-69, 76-93, and 95-103 of the '740 Patent. The Defendants have failed to provide sufficient evidence to support their defenses to these claims of infringement. Summary Judgment is, therefore, granted in favor of Terves on these specific claims. Terves has also shown that the accused products infringe claims 1, 4, 5, 7, 12, 13, 25, 29, 33, 37, 41, 43, 45,

**THE UNITED STATES DISTRICT COURT
NORTHERN DISTRICT OF OHIO
EASTERN DIVISION**

TERVES LLC,

Plaintiff,

V.

**YUEYANG AEROSPACE NEW
MATERIALS CO., LTD., *et al.*,**

Defendants.

CASE NO. 1: 19 CV 1611

JUDGE DONALD C. NUGENT

JUDGMENT

The above-captioned case came before this Court for a trial by jury. At the conclusion of the trial, the Jury unanimously answered two interrogatories finding that Plaintiff proved by a preponderance of the evidence that Defendants' infringement of the '653 patent and/or the '740 patent (collectively "the Terves patents") was not willful and finding Plaintiff proved lost profit damages in the amount of \$707,207.00.

Plaintiff Terves, LLC brought this patent action against Defendants, Yueyang Aerospace New Materials Co., Ltd, Ecometal, Inc., and Nick Yuan alleging that Defendants infringed numerous claims in the Terves patents by importing, using, selling, and/or offering for sale dissolvable cast magnesium alloys. In an earlier summary judgment ruling the Court determined that claims 2, 3, 9, 14, 15, 18-20, 23, 26, 27, 30, 31, 34, 35, 38, 39, 42, 46-47, 50, 52-54, 56-61, 64, 66, 67, and 76 of the '653 patent and claims 3-5, 8-11, 13, 16-17, 20-47, 51-69, 76-93, and 95-103 of the '740 patent were valid and patentable and that Defendants Ecometal and Yuan infringed those claims by importing, using, selling, and/or offering for sale dissolvable cast

magnesium.¹ (See ECF #178) The case proceeded to trial on the issues of what money damages, if any, should be awarded to Plaintiff to compensate it for the infringement, and to determine whether the infringement was willful.

The trial commenced on April 22, 2022 at 8:00 a.m. Defendant Yueyang Materials Co., Ltd., was dismissed without prejudice pursuant to Plaintiff's request. Ecometal's Counterclaim #1 was dismissed at Ecometal's request. A Jury of twelve was duly empaneled and sworn, and opening statements of counsel were made. Plaintiff called the following witnesses: (1) Andrew J. Sherman. Court was adjourned until April 25, 2022 at 8:00 a.m.

The trial continued on April 25, 2022. Plaintiff called the following witness(es): (2) Brian Doud; and (3) Ying Hong Yuan. Court was adjourned until April 26, 2022 at 8:00 a.m.

The trial continued on April 26, 2022. Plaintiff called the following witness(es): (4) David Haas. Plaintiff rested. Defendants' motion pursuant to Fed. R. Civ. P. 50 was denied. Defendants called the following witness(es): (1) Dr. Dana James Medlin. Defendants rested. Plaintiff rested. Court was adjourned until April 27, 2022 at 8:00 a.m.

The trial continued on April 27, 2022. The Court gave initial instructions of law to the Jury. Closing arguments of counsel were made. The Court gave final instructions of law to the Jury and the Jury retired to deliberate. The Jury, in open court, returned the following unanimous Interrogatory answers pursuant to Rule 49 of the Federal Rules of Civil Procedure:

1

Defendant Yueyang Aerospace New Materials Co., Ltd., a Chinese company, never participated in the case and service through the Hague convention may not have been completed.

INTERROGATORY NO. 1

Did Terves, LLC prove by a preponderance of the evidence, that Defendants' infringement of the '653 and/or the '740 Patent was willful?

_____ Yes X no

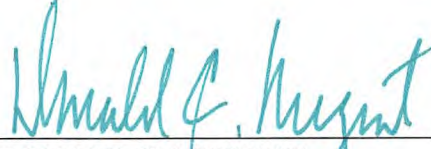
INTERROGATORY NO. 2

We the jury find, by a preponderance of the evidence, that Plaintiff has proven lost profit damages in the amount of \$707,207.00 (insert in ink an amount from \$0 to whatever the evidence requires)

The Court read the Interrogatory Answers in open court, and thereafter, the Court polled the Jury. Each Juror affirmatively responded to the correctness of the Interrogatory Answers. The Court accepted the Interrogatory Answers. The Jury was then discharged. THEREFORE, the Court enters Judgment pursuant to Rule 58 of the Federal Rules of Civil Procedure finding that Defendants' infringement of the claims at issue was not willful and awarding Plaintiff compensatory damages against Defendants Ecometal, Inc. and Nick Yuan on Plaintiff's claims of infringement in the amount of \$707,207.00. All costs, including all jury charges, are to be paid by Defendants.

IT IS SO ORDERED.

DATE: April 28, 2022


DONALD C. NUGENT
UNITED STATES DISTRICT JUDGE

UNITED STATES DISTRICT COURT
NORTHERN DISTRICT OF OHIO
EASTERN DIVISION

TERVES LLC,)	
)	Case No. 1:19-CV-1611
Plaintiff,)	
)	
v.)	JUDGE DONALD C. NUGENT
)	
YUEYANG AEROSPACE NEW)	
MATERIALS CO., LTD., <i>et al.</i> ,)	
)	<u>MEMORANDUM OPINION</u>
Defendants.)	<u>AND ORDER</u>
)	

This matter is before the court on the Plaintiff, Terves LLC’s Motion for Permanent Injunction. (ECF #211). The motion asks this Court to issues a permanent injunction enjoining Defendants from importing, making, using, selling, and/or offering to sell any of the infringing materials, or any material covered by the infringed claims, as well as any product manufactured from infringing material. Defendants filed an Opposition to the motion, and Plaintiff filed a Reply in support of its motion. (ECF # 216, 217). This issue is now ready for disposition.

The Patent Act provides that in cases of patent infringement a court “may grant injunctions in accordance with the principles of equity to prevent the violation of any right secured by the patent, on such terms as the court deems reasonable.” 35 U.S.C. §283. A permanent injunction is warranted when the patentee can show: (1) that it has suffered an irreparable injury; (2) that remedies available at law, such as monetary damages, are inadequate to compensate for that injury; (3) that, considering the balance of hardships between the plaintiff and defendant, a remedy in equity is warranted; and (4) that the public interest would not be disserved by a permanent injunction. *eBay Inc. v.*

MerchExchange, LLC, 547 U.S. 388, 391 (2006). Though the irreparable injury was once presumed in patent cases where infringement had been established, the Federal Circuit has held that the eBay case cited above “jettisoned the presumption of irreparable harm.” The decision to grant or deny permanent injunctive relief is an act of equitable discretion by the district court. . .” *eBay*, 547 U.S. at 391.

A. Ecometal/Nick Yuan

1. Irreparable Harm/Inadequate Remedy at Law

When determining whether the a permanent injunction is warranted in a patent case, the first two factors, irreparable harm and inadequate remedy at law, may be considered together. *See generally, Acumed LLC v. Stryker Corp.*, 551 F.3d 1323, 1327-29 (Fed. Cir. 2008). A harm is irreparable when there there is no fully adequate remedy at law. *See Daimler AG v. A-Z Wheels LLC*, 498 F.Supp. 3d 1282, 1293-94 (S.D. Cal. 2020). Although there is no longer a presumption that an injunction should issue whenever infringement is found, Courts still issue permanent injunctions in the great majority of cases where, as is the case here, the patent owner and the infringer are in direct competition. *See, Seaman, C., Permanent Injunctions in Patent Litigation After eBay: An Empirical Study*, 1010 Iowa L. Rev. 1949, 1990-91 (2016). Indeed, subsequent to the *eBay* opinion, the Federal Circuit has noted that “[c]ourts awarding permanent injunctions typically do so under circumstances where plaintiff practices its invention and is a direct market competitor,” and that patent owners who sell their own product “may normally expect to regain the exclusivity that was lost with the infringement,” *Edwards Lifesciences AG v. CoreValve, Inc.*, 699 F.3d 1305,1314 (quoting *Advanced Cardiovascular Sys. Medtronic Vascular, Inc.*, 579 F.Supp.2d 554, 558 (D. Del. 2008)).

The mere fact that Terves was awarded money damage for prior infringement does not mean that these damages were adequate to fully address the harm caused by Ecometal’s infringement. In this case, both Terves and the Ecometal Defendants (“Ecometal”) sell billets made up of the patented dissolvable cast magnesium. Terves also sells frac plugs and balls made of this patented material. These products directly compete with frac plugs and balls sold by Magnesium Machine LLC (“MMP”), made with the infringing material, which MMP obtains from Ecometal. Direct competition between a patent owner and an infringer creates a unique harm that cannot be fully addressed by recovery of lost profits. “Where two companies are in competition against one another, the patentee suffers the harm – often irreparable – of being forced to compete against products that incorporate and infringe its own patented inventions.” *Douglas Dynamics, LLC v. Buyers Products Co.*, 717 F.3d 1336, 1345 (Fed. Cir. 2013)(reversing denial of permanent injunction). Sales lost to infringing competitors can cause lost market share, loss of value gained by economies of scale and exclusivity, price erosion, and lost or diminished business relationships and reputation leading to lost references and repeat sales. This is particularly true when, as here, the market is small,¹ the infringer has developed relationships with the downstream customers and provides the patented product at a lower price and, the patented product is the core of the plaintiff’s business. *See, e.g., TEK Global, S.R.L. v. Sealant Sys. Int’l Inc.*, 920 F.3d 777, 792 (Fed. Cir. 2019); *Metalcraft of Mayville Inc. v. The Toro Co.*, 848 F.3d 1358, 1368 (Fed. Cir. 2017); *Celcis in Vitro, Inc. v. CellzDirect, Inc.*, 664 F.3d 922, 930 (Fed. Cir. 2012).

¹ Terves has also presented evidence that would show that the market for its product “consists of only a few large customers,” and therefore, “the loss of a single customer can have a devastating and irreparable impact on Terves.” Ecometal, itself admits that four producers of fracking plugs and balls, potential customers for Terves’ billets, make up 72% of the entire market.

Ecometal argues that sales lost to an infringing product cannot irreparably harm a patentee if the demand for the product is not “tied to the intrinsic value of the patented feature,” *Calico Brand, Inc. v. Ameritek Imps., Inc.*, 527 F.App’x 987, 996 (Fed. Cir. 2013), or if sales would be lost regardless of the infringing product. *Apple Inc. v. Samsung Elecs. Co.*, 735 F.3d 1352, 1359-60 (Fed. Cir. 2013). However, Ecometal does not even attempt to tie this argument to its sale of the infringing dissolvable magnesium billets or balls. It focuses solely an alleged value in the specific design of fracking plugs sold not by Ecometal, but by MMP.

Ecometal’s argument that neither Terves nor MMP is a top supplier of fracking plugs and balls has no relevance to whether Ecometal’s sale of infringing material to such suppliers would be likely to cause Terves irreparable harm. First of all, the product Ecometal would be enjoined from selling is the dissolvable magnesium, or billets. Further, the fact that other infringers may remain in the marketplace, does not preclude a finding of irreparable harm should Ecometal continue to sell infringing products. *See, Robert Bosch LLC, Pylon Mfg. Corp.*, 659 F.3d 1142, 1148 (Fed. Cir. 2011). Ecometal’s argument that the Court could force the parties into a licensing agreement fares no better. Terves has stated that it does not intend to license the product to Ecometal, and absent any desire to negotiate a licensing agreement, future sales by Ecometal would result in further infringement, further dilution of the market share, further expense in policing and enforcing Terves’ patents, and further challenges to its customer relationships. Terves is not required to license its product. It is entitled to the benefit of exclusivity and exclusion, which is “a fundamental tenet of patent law.” *Edwards Lifescience*, 699 F.3d at 1314 (quoting *Advanced Cardiovascular Sys. Medtronic Vascular, Inc.*, 579 F.Supp. 2d 554, 558 (D. Del. 2008)).

Finally, Ecometal argues that there is no risk of future irreparable harm because Defendants' shipments of infringing products have ceased and there is no intent to ship infringing material in the future. In their eyes, absent evidence of future infringement, a permanent injunction is not warranted. However, the issuance of a permanent injunction is intended to prevent future infringement. It cannot, therefore, be reliant on plaintiff's ability to present "evidence of future infringement." Further, neither Terves nor the Court should be expected to rely solely on the Defendants' unilateral promise that infringement will cease.

2. Balance of Hardships

The balance of hardships weighs strongly in favor of an injunction. Ecometal will not be unfairly prejudiced by an injunction preventing them from illegally infringing materials. Nick Yuan has indicated that he does not intend to sell this product in the future and that he also sells other non-infringing products. Further, he has no employees and no capital investments at stake. He simply imports the material into his home, and delivers its out to a single other downstream customer. Any reputational harm that might arise from the issuance of a permanent injunction is negligible considering that there is already a jury finding of infringement and a monetary judgment against him in connection with the same product.

On the other hand for all of the reasons set forth in the section above, Terves would suffer not only monetary but other irreparable harm if the infringing product continues to make its way into the marketplace. There was testimony at trial that the loss of sales and customers attributable to the availability of the infringing product caused hardship to Terves and its employees. Terves had to

furlough and layoff employees in 2019 and 2020 due to reduced demand, and the equipment and manufacturing investments it made to increase production have remained underutilized.

3. Public Interest

The Federal Circuit has held that the “public interest nearly always weighs in favor of protecting property rights in the absence of countervailing factors, especially when the patentee practices his inventions.” *Apple Inc. v. Samsung Elecs. Co., Ltd.*, 809 F.3d 633, 647 (Fed. Cir. 2015). There is no evidence in this case of any countervailing factors. Terves has demonstrated that it has the capacity to supply Ecometal’s and/or MMP’s customers with the patented product and its derivatives. There is no reason to believe that the market, or the general public would be adversely affected in any way.

B. Magnesium Machine LLP

Ecometal argues that any injunction issued should not properly include MMP, because MMP is not a party to this action. “[A]n injunction ordinarily cannot be imposed on a non-party that has not had the opportunity to contest its liability.” *Additive Controls & Measurement Sys., Inc. v. Flowdata, Inc.*, 96 F.3d 1390, 1397 (Fed. Cir. 1996). The Federal Circuit has allowed injunctions to stand against non-parties if they are “in active concert or participation” with the infringers, which has been interpreted to mean “assisting the enjoined party in violating the injunction.” Injunctions against non-parties should not be issued to prevent alleged infringing activity that is independent of the conduct alleged against the named defendant. “If [the plaintiff] wishes to obtain permanent injunctive relief against [a non-party] based on their independent activities, it cannot do so by seeking an injunction against them in a case to which they are not parties; it must, instead, validly serve them and obtain an adjudication of infringement against them.” *Additive Controls*, 96 F.3d at

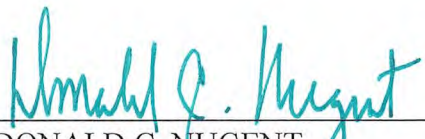
1397. A court may, however, issue an injunction against a non-party to prohibit complicity with an enjoined infringer. *Id.*

There is evidence that MMP and Ecometal have an exclusivity agreement requiring Ecometal to sell the infringing product only to MMP, and allowing MMP to purchase this material only from Ecometal. The agreement also provides that MMP pay half of Ecometals defense fees in this case. MMP and Ecometal share the same attorneys, and Ecometal identified MMP as a “real party in interest” during the IPR proceedings at the U.S. Patent Office due to the nature of their exclusive relationship. Because of the nature of their relationship, MMP may be enjoined from participating or acting in concert with Ecometal to purchase or sell infringing product. It would not be appropriate, however, to enjoin MMP from any independent conduct, whether or not that conduct is alleged to constitute infringement.

There is insufficient evidence in this case to establish that a permanent injunction is warranted prohibiting the sale of any product (e.g., frac plug, ball, or other tool) manufactured from the Infringing Materials purchased from Ecometal prior to the judgment in this case. The jury in this case considered evidence including the value of the infringing materials and the MMP products manufactured from these materials, and were able to take these into account in formulating their judgment and award. Further, MMP has not had an opportunity to address the causal nexus requirement and it has not been determined whether other non-accused components of MMP’s products might be the primary driver of its sales and market position. *See, Calico Brand, Inc. V. Ameritek Imps., Inc.*, 527 F. App’x 987, 996 (Fed. Cir. 2013); *Apple Inc.*, 735 F.3d at 1324. However, any future purchase of the infringing materials from Ecometal would constitute active participation in Ecometals’ infringement, and is, therefore, subject to injunction.

For the reasons set forth above, the court hereby issues a permanent injunction against Ecometal Inc. and Nick Yuan, and their privies, assignees, officers, agents, attorneys, employees, representatives, principals, and associates, until the expiration of both the '653 and '740 Patents from: (1) importing, making, using, selling, and/or offering to sell any of the Infringing Materials, defined as AJM-006, AJM-010, AJM-012, AJM-016, AJM-017, AJM-018, and AJM-023, which the Court found infringing in its summary judgment ruling, whether or not those products maintain the same product numbers going forward; and, (2) importing, making, using, selling, and/or offering to sell any material that is covered by any of the Infringed Claims, defined as Claims 2, 3, 9, 14, 15, 18-20, 23, 26, 27, 30, 31, 34, 35, 38, 39, 42, 46, 47, 50, 52-54, 56-61, 64, 66, 67, and 76 of the '653 Patent and claims 3-5, 8-11, 13, 16, 17, 20-47, 51-69, 76-93, and 95-103 of the '740 Patent. Magnesium Machine LLC is also permanently enjoined from purchasing any infringing product, as defined above, from any of the Defendants, or from otherwise participating or acting in concert with Ecometal or Nick Yuan to violate the terms of this injunction.

IT IS SO ORDERED.


DONALD C. NUGENT
UNITED STATES DISTRICT JUDGE

Date: July 20, 2022

UNITED STATES DISTRICT COURT
NORTHERN DISTRICT OF OHIO
EASTERN DIVISION

TERVES LLC,)	
)	Case No. 1:19-CV-1611
Plaintiff,)	
)	
v.)	JUDGE DONALD C. NUGENT
)	
YUEYANG AEROSPACE NEW)	
MATERIALS CO., LTD., <i>et al.</i> ,)	
)	
Defendants.)	<u>ORDER</u>
)	

The above-captioned case came before this Court for a trial by jury from April 22, 2022, until April 27, 2022. At the conclusion of the trial, the Jury unanimously answered two interrogatories finding that (a) plaintiff Terves, LLC proved by a preponderance of the evidence lost profit damages in the amount of \$707,207.00 against Defendants Ecometal Inc. and Nick Yuan for their infringement of Terves' U.S. Patent Nos. 10,329,653 (the "'653 patent") and 10,689,740 (the "'740 patent"); and, (b) Terves had not proven by a preponderance of evidence that defendants' infringement was willful. (ECF #203). The judgment was later revised to include costs, fees, and pre-judgment interest, bringing the total award to \$793,699.49. (ECF #218).

In an earlier summary judgment ruling, the Court ruled that claims 2, 3, 9, 14, 15, 18-20, 23, 26, 27, 30, 31, 34, 35, 38, 39, 42, 46-47, 50, 52-54, 56-61, 64, 66, 67, and 76 of the '653 patent and claims 3-5, 8-11, 13, 16, 17, 20-47, 51-69, 76-93, and 95-103 of the '740 patent (the

“Infringed Claims) were valid, enforceable, and patentable. The Court also ruled that Ecometal’s dissolvable cast magnesium products, specifically AJM-006, AJM-010, AJM-012, AJM-016, AJM-017, AJM-018, and AJM -023 (the “Infringing Materials”) infringe the above Claims, and that Defendants Ecometal and Yuan infringed the Infringed Claims by importing, using, selling, and/or offering for sale each of the Infringing Materials. (ECF #178).

On May 10, 2022, Terves moved for a permanent injunction. (ECF #211). Having now considered that motion and all related briefing and evidence, the Court hereby GRANTS the Motion and enters the following Permanent Injunction.

IT IS HEREBY ORDERED, ADJUDGED, AND DECREED as follows:

1. Ecometal Inc., Nick Yuan, and their privies, assignees, officers, agents, attorneys, employees, representatives, principals, and associates, and those in active concert or participation with them who receive actual notice of this Injunction are enjoined and restrained, collectively and individually, until the expiration of both the ’653 and ’740 patents from:


(A) importing, making, using, selling, and/or offering to sell any of the Infringing Materials;
(B) importing, making, using, selling, and/or offering to sell any material that is covered by any of the Infringed Claims.

2. As it has been found that any future purchase of Infringing Materials from the Defendants in this case by Magnesium Machine, LLC, would constitute active participation in Ecometal’s infringing conduct, Magnesium Machine is also permanently enjoined from purchasing any Infringing Materials, or any material covered by the Infringed Claims from Ecometal, Nick Yuan, or

Yueyang Aerospace New Materials Co. Ltd.; and from otherwise participating or acting in concert with these entities to violate the terms of this injunction.

Ecometal Inc. and Nick Yuan shall send written notice of this Injunction, by copy thereof, to all of their past and present downstream customers who have purchased the Infringing Materials from them, including Magnesium Machine, LLC.

IT IS SO ORDERED.


DONALD C. NUGENT
UNITED STATES DISTRICT JUDGE

Date:

July 20, 2022

(12) **United States Patent**
Doud et al.

(10) **Patent No.:** **US 10,329,653 B2**

(45) **Date of Patent:** ***Jun. 25, 2019**

(54) **GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS**

(58) **Field of Classification Search**

CPC ... C22F 1/06; C22C 23/02; C22C 1/02; C22C 23/00

See application file for complete search history.

(71) Applicant: **Terves Inc.**, Euclid, OH (US)

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(Continued)

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(Continued)

Primary Examiner — Anthony J Zimmer

(74) Attorney, Agent, or Firm — Fay Sharpe LLP

(57)

ABSTRACT

A castable, moldable, and/or extrudable structure using a metallic primary alloy. One or more additives are added to the metallic primary alloy so that in situ galvanically-active reinforcement particles are formed in the melt or on cooling from the melt. The composite contain an optimal composition and morphology to achieve a specific galvanic corrosion rate in the entire composite. The in situ formed galvanically-active particles can be used to enhance mechanical properties of the composite, such as ductility and/or tensile strength. The final casting can also be enhanced by heat treatment, as well as deformation processing such as extrusion, forging, or rolling, to further improve the strength of the final composite over the as-cast material.

78 Claims, 4 Drawing Sheets

(73) Assignee: **Terves Inc.**, Euclid, OH (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 29 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **15/641,439**

(22) Filed: **Jul. 5, 2017**

(65) **Prior Publication Data**

US 2017/0298492 A1 Oct. 19, 2017

Related U.S. Application Data

(62) Division of application No. 14/689,295, filed on Apr. 17, 2015, now Pat. No. 9,903,010.

(Continued)

(51) **Int. Cl.**

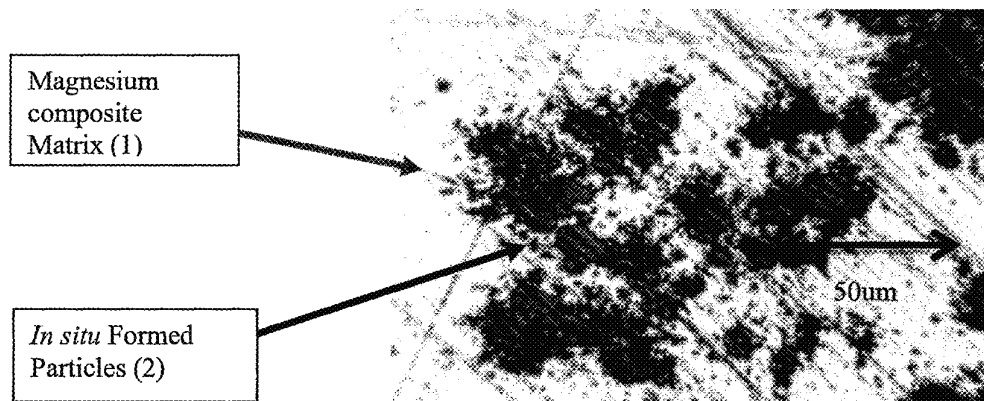
C22C 1/02 (2006.01)

C22F 1/06 (2006.01)

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CPC **C22F 1/06** (2013.01); **C22C 1/02** (2013.01); **C22C 23/02** (2013.01); **C22C 23/00** (2013.01)



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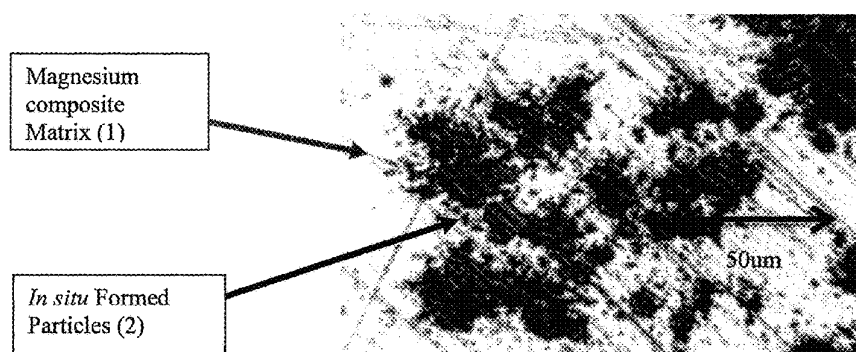


FIG 1.

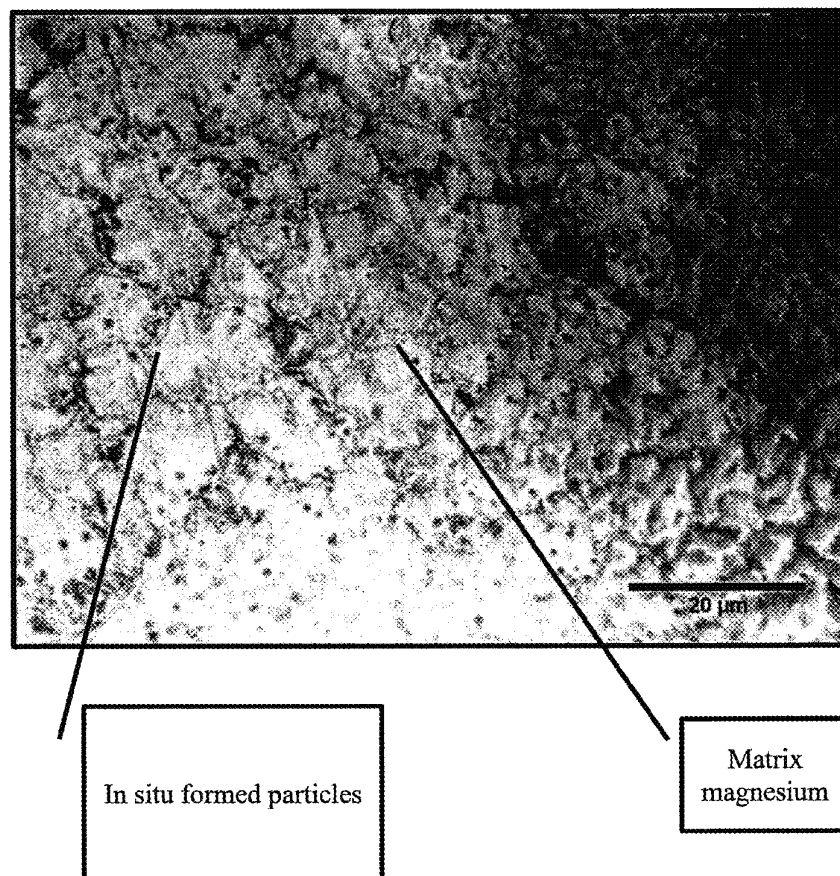


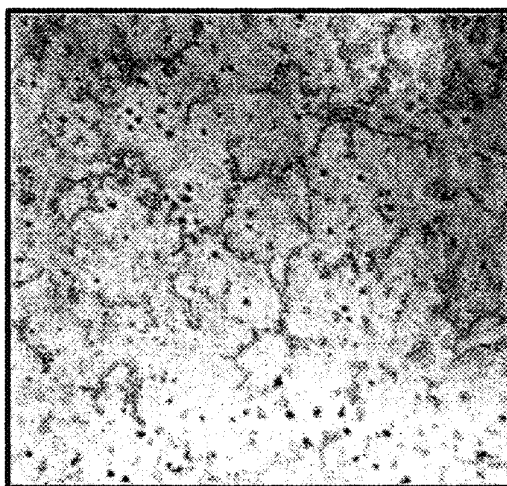
FIG. 2

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Highlighted In Situ Formed Particles

FIG. 3

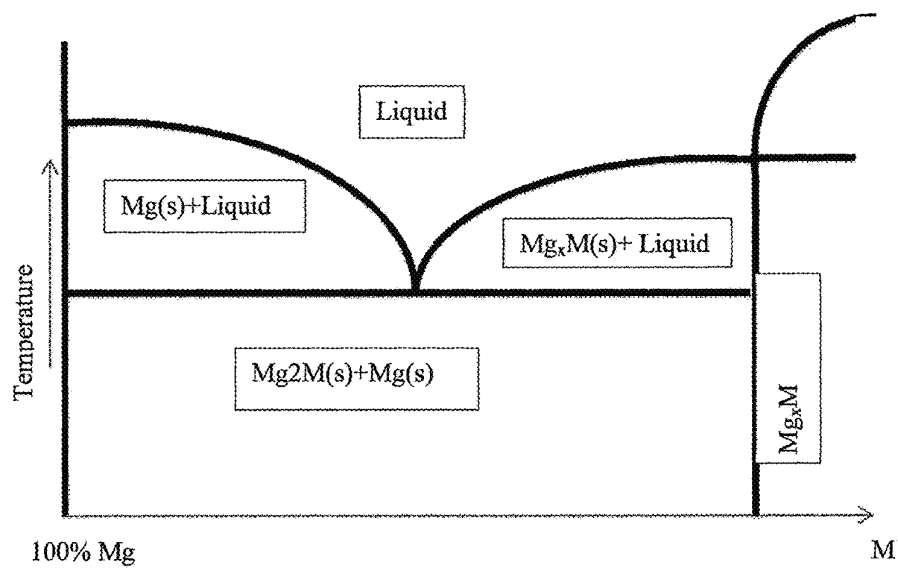


FIG. 4

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GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS

The present invention is a divisional of U.S. patent application Ser. No. 14/689,295 filed Apr. 17, 2015, which in turn claims priority on U.S. Provisional Patent Application Ser. No. 61/981,425 filed Apr. 18, 2014, which is incorporated herein by reference.

FIELD OF THE INVENTION

The present invention is directed to a novel magnesium composite for use as a dissolvable component in oil drilling.

BACKGROUND OF THE INVENTION

The ability to control the dissolution of a down hole well component in a variety of solutions is very important to the utilization of non-drillable completion tools, such as sleeves, frac balls, hydraulic actuating tooling, and the like. Reactive materials for this application, which dissolve or corrode when exposed to acid, salt, and/or other wellbore conditions, have been proposed for some time. Generally, these components consist of materials that are engineered to dissolve or corrode. Dissolving polymers and some powder metallurgy metals have been disclosed, and are also used extensively in the pharmaceutical industry for controlled release of drugs. Also, some medical devices have been formed of metals or polymers that dissolve in the body.

While the prior art well drill components have enjoyed modest success in reducing well completion costs, their consistency and ability to specifically control dissolution rates in specific solutions, as well as other drawbacks such as limited strength and poor reliability, have impacted their ubiquitous adoption. Ideally, these components would be manufactured by a process that is low cost, scalable, and produces a controlled corrosion rate having similar or increased strength as compared to traditional engineering alloys such as aluminum, magnesium, and iron. Ideally, traditional heat treatments, deformation processing, and machining techniques could be used on the components without impacting the dissolution rate and reliability of such components.

SUMMARY OF THE INVENTION

The present invention is directed to a novel magnesium composite for use as a dissolvable component in oil drilling and will be described with particular reference to such application. As can be appreciated, the novel magnesium composite of the present invention can be used in other applications (e.g., non-oil wells, etc.). In one non-limiting embodiment, the present invention is directed to a ball or other tool component in a well drilling or completion operation such as, but not limited to, a component that is seated in a hydraulic operation that can be dissolved away after use so that no drilling or removal of the component is necessary. Tubes, valves, valve components, plugs, frac balls, and other shapes and components can "also be formed of the novel magnesium composite of the present invention. For purposes of this invention, primary dissolution is measured for valve components and plugs as the time the part removes itself from the seat of a valve or plug arrangement or can become free floating in the system. For example, when the part is a plug in a plug system, primary dissolution occurs when the plug has degraded or dissolved to a point

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that it can no longer function as a plug and thereby allows fluid to flow about the plug. For purposes of this invention, secondary dissolution is measured in the time the part is fully dissolved into sub-mm particles. As can be appreciated, the novel magnesium composite of the present invention can be used in other well components that also desire the function of dissolving after a period of time. In one non-limiting aspect of the present invention, a galvanically-active phase is precipitated from the novel magnesium composite composition and is used to control the dissolution rate of the component; however, this is not required. The novel magnesium composite is generally castable and/or machinable, and can be used in place of existing metallic or plastic components in oil and gas drilling rigs including, but not limited to, water injection and hydraulic fracturing. The novel magnesium composite can be heat treated as well as extruded and/or forged.

In one non-limiting aspect of the present invention, the novel magnesium composite is used to form a castable, moldable, or extrudable component. Non-limiting magnesium composites in accordance with the present invention include at least 50 wt. % magnesium. One or more additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention. The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives typically are added in a weight percent that is less than a weight percent of said magnesium or magnesium alloy. Typically, the magnesium or magnesium alloy constitutes about 50.1 wt % to 99.9 wt % of the magnesium composite and all values and ranges therebetween. In one non-limiting aspect of the invention, the magnesium or magnesium alloy constitutes about 60 wt. %-95 wt. % of the magnesium composite, and typically the magnesium or magnesium alloy constitutes about 70 wt. %-90 wt. % of the magnesium composite. The one or more additives are typically added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives. The one or more additives generally have an average particle diameter size of at least about 0.1 microns, typically no more than about 500 microns (e.g., 0.1 microns, 0.1001 microns, 0.1002 microns . . . 499.9998 microns, 499.9999 microns, 500 microns) and including any value or range therebetween, more typically about 0.1 to 400 microns, and still more typically about 10 to 50 microns. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are typically not caused to fully melt in the molten magnesium or magnesium alloy. As can be appreciated, the one or more additives can be added to the molten magnesium or magnesium alloy at a temperature that is greater than the melting point of the one or more additives. In such a method of forming the magnesium composite, the one or more additives form secondary metallic alloys with the magnesium and/or other metals in the magnesium alloy, said secondary metallic alloys having a melting point that is greater than the magnesium and/or other metals in the magnesium alloy. As the molten metal cools, these newly formed secondary metallic alloys begin to precipitate out of the molten metal and form the in situ phase to the matrix phase in the cooled and solid magnesium composite. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten

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magnesium or magnesium alloy are cooled to form a solid component. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 10° C. less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process, typically at least about 100° C. less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process, more typically about 100° C.-1000° C. (and any value or range therebetween) less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required. The never melted particles and/or the newly formed secondary metallic alloys are referred to as in situ particle formation in the molten magnesium composite. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite.

The invention adopts a feature that is usually a negative in traditional casting practices wherein a particle is formed during the melt processing that corrodes the alloy when exposed to conductive fluids and is imbedded in eutectic phases, the grain boundaries, and/or even within grains with precipitation hardening. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the in situ phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The in situ formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the in situ formed particles size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of in situ particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. In situ particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques.

In another non-limiting aspect of the invention, a cast structure can be made into almost any shape. During formation, the active galvanically-active in situ phases can be uniformly dispersed throughout the component and the grain or the grain boundary composition can be modified to achieve the desired dissolution rate. The galvanic corrosion can be engineered to affect only the grain boundaries and/or can affect the grains as well (based on composition); however, this is not required. This feature can be used to enable

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fast dissolutions of high-strength lightweight alloy composites with significantly less active (cathode) in situ phases as compared to other processes.

In still another and/or alternative non-limiting aspect of the invention, ultrasonic processing can be used to control the size of the in situ formed galvanically-active phases; however, this is not required.

In yet another and/or alternative non-limiting aspect of the invention, the in situ formed particles can act as matrix strengtheners to further increase the tensile strength of the material compared to the base alloy without the additive; however, this is not required.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method of controlling the dissolution properties of a metal selected from the class of magnesium and/or magnesium alloy comprising of the steps of a) melting the magnesium or magnesium alloy to a point above its solidus, b) introducing an additive material and/or phase to the magnesium or magnesium alloy in order to achieve in situ precipitation of galvanically-active intermetallic phases, and c) cooling the melt to a solid form. The additive material is generally added to the magnesium or magnesium alloy when the magnesium or magnesium alloy is in a molten state and at a temperature that is less than the melting point of the additive material. The galvanically-active intermetallic phases can be used to enhance the yield strength of the alloy; however, this is not required. The size of the in situ precipitated intermetallic phase can be controlled by a melt mixing technique and/or cooling rate; however, this is not required. The method can include the additional step of subjecting the magnesium composite to intermetallic precipitates to solutionizing of at least about 300° C. to improve tensile strength and/or improve ductility; however, this is not required. The solutionizing temperature is less than the melting point of the magnesium composite. Generally, the solutionizing temperature is less than 50° C.-200° C. (the melting point of the magnesium composite) and the time period of solutionizing is at least 0.1 hours. In one non-limiting aspect of the invention, the magnesium composite can be subjected to a solutionizing temperature for about 0.5-50 hours (e.g., 1-15 hours, etc.) at a temperature of 300° C.-620° C. (e.g., 300° C.-500° C., etc.). The method can include the additional step of subjecting the magnesium composite to intermetallic precipitates and to artificially age the magnesium composite at a temperature at least about 90° C. to improve the tensile strength; however, this is not required. The artificially aging process temperature is typically less than the solutionizing temperature and the time period of the artificially aging process temperature is typically at least 0.1 hours. Generally, the artificially aging process is less than 50° C.-400° C. (the solutionizing temperature). In one non-limiting aspect of the invention, the magnesium composite can be subjected to aging treatment for about 0.5-50 hours (e.g., 1-16 hours, etc.) at a temperature of 90° C.-300° C. (e.g., 100° C.-200° C.).

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-35 wt. % nickel (and all values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic Mg₂Ni as a galvanically-active in situ precipitate. In one non-limiting arrangement, the magnesium composite includes about 0.05-23.5 wt. % nickel, 0.01-5 wt. % nickel, 3-7 wt. % nickel, 7-10 wt. % nickel, or 10-24.5 wt. % nickel. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout

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the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an in situ precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-35 wt. % copper (and all values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic $CuMg_2$ as the galvanically-active in situ precipitate. In one non-limiting arrangement, the magnesium composite includes about 0.01-5 wt. % copper, about 0.5-15 wt. % copper, about 15-35 wt. % copper, or about 0.01-20 wt. %. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of $CuMg_2$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $CuMg_2$, and any unalloyed copper particles are cooled and an in situ precipitate of solid particles of $CuMg_2$ and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the copper added to the molten magnesium or magnesium alloy.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-20% by weight cobalt is added to the magnesium or magnesium alloy to form an intermetallic $CoMg_2$ as the galvanically-active in situ precipitate. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. During the mixing process, solid particles of $CoMg_2$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $CoMg_2$, and any unalloyed cobalt particles are cooled and an in situ precipitate of solid particles of $CoMg_2$ and any unalloyed cobalt particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the cobalt added to the molten magnesium or magnesium alloy.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and cobalt is added to the magnesium or magnesium alloy which forms an intermetallic Mg_2Co as the galvanically-active particle in situ precipitate. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the

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cobalt. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. During the mixing process, solid particles of $CoMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $CoMg_x$, and any unalloyed cobalt particles are cooled and an in situ precipitate of solid particles of $CoMg_x$ and any unalloyed cobalt particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the cobalt added to the molten magnesium or magnesium alloy.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.5-35% by weight of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 1° C. per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $SMMg_x$, and any unalloyed secondary metal particles are cooled and an in situ precipitate of solid particles of $SMMg_x$ and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.5-35% by weight of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is slower than 1° C. per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $SMMg_x$, and any unalloyed secondary metal particles are cooled and an in situ precipitate of solid particles of $SMMg_x$ and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that

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is over 50 wt. % magnesium and about 0.05-35 wt. % of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 0.01° C. per min and slower than 1° C. per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of SMMg_x are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of SMMg_x, and any unalloyed secondary metal particles are cooled and an in situ precipitate of solid particles of SMMg_x, and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-35 wt. % of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 10° C. per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of SMMg_x were formed. Once the mixing process was completed, the mixture of molten magnesium or magnesium alloy, solid particles of SMMg_x, and any unalloyed secondary metal particles are cooled and an in situ precipitate of solid particles of SMMg_x, and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided magnesium composite that is over 50 wt. % magnesium and about 0.5-35 wt. % of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is slower than 10° C. per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of SMMg_x are formed.

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Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of SMMg_x, and any unalloyed secondary metal particles are cooled and an in situ precipitate of solid particles of SMMg_x and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium alloy that includes over 50 wt. % magnesium and includes at least one metal selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.05-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, and/or manganese in an amount of about 0.15-2 wt. %. In one non-limiting formulation, the magnesium alloy that includes over 50 wt. % magnesium and includes at least one metal selected from the group consisting of zinc in amount of about 0.05-6 wt. %, zirconium in an amount of about 0.05-3 wt. %, manganese in an amount of about 0.05-0.25 wt. %, boron in an amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %. The magnesium alloy can then be heated to a molten state and one or more secondary metal (SM) (e.g., copper, nickel, cobalt, titanium, silicon, iron, etc.) can be added to the molten magnesium alloy which forms an intermetallic galvanically-active particle in situ precipitate. The galvanically-active particle can be SMMg_x, SMAl_x, SMZn_x, SMZr_x, SMMn_x, SMB_x, SMBi_x, SM in combination with anyone of B, Bi, Mg, Al, Zn, Zr, and Mn.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and at least one metal selected from the group consisting of zinc in an amount of about 0.05-6 wt. %, zirconium in amount of about 0.05-3 wt. %, manganese in an amount of about 0.05-0.25 wt. %, boron in an amount of about 0.0002-0.04 wt. %, and/or bismuth in an amount of about 0.4-0.7 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The magnesium alloy can then be heated to a molten state and one or more secondary metal (SM) (e.g., copper, nickel, cobalt, titanium, iron, etc.) can be added to the molten magnesium alloy which forms an intermetallic galvanically-active particle in situ precipitate. The galvanically-active particle can be SMMg_x, SMZn_x, SMZr_x, SMMn_x, SMB_x, SMBi_x, SM in combination with anyone of Mg, Zn, Zr, Mn, B and/or Bi.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium or magnesium alloy that is over 50 wt. % magnesium and nickel in an amount of about 0.01-5 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg₂Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg₂Ni, and any unalloyed nickel particles are cooled and an in situ precipitate of solid particles of Mg₂Ni and any unalloyed nickel particles are formed in the solid magne-

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In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and nickel in an amount of about 10-24.5 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an in situ precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the

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In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and includes copper in an amount of about 15-35 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Cu , and any unalloyed nickel particles are cooled and an in situ precipitate of solid particles of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°

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C. less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and includes copper in an amount of about 0.01-20 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Cu , and any unalloyed nickel particles are cooled and an in situ precipitate of solid particles of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The aging process (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours. The solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content is at least about 75% and nickel is added to form in situ precipitation of at least 0.05 wt. % $MgNi_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without nickel additions subjected to the said aging treatment.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the magnesium content is at least about 85% and nickel is added to form in situ precipitation of at least 0.05 wt. % $MgNi_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature at about 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of nickel.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content in the alloy is at least about 75% and copper is added to form in situ precipitation of at least about 0.05 wt. % $MgCu_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. for a period of 0.25-50 hours, the

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magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said aging treatment.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the total content of magnesium in the magnesium or magnesium alloy is at least about 85 wt. % and copper is added to form in situ precipitation of at least 0.05 wt. % $MgCu_2$ with the magnesium or magnesium composite and solutionizing the resultant metal at a temperature of about 100-500° C. for a period of 0.25-50 hours, the magnesium composite is characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of copper.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable ball or frac ball in hydraulic fracturing and well drilling.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable tool for use in well drilling and hydraulic control as well as hydraulic fracturing.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes secondary institute formed reinforcements that are not galvanically-active to the magnesium or magnesium alloy matrix to increase the mechanical properties of the magnesium composite. The secondary institute formed reinforcements include a Mg_2Si phase as the in situ formed reinforcement.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a faster cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a slower cooling rate from the liquidus to the solidus point to create larger in situ formed particles.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The aging process (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours. The solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content is at least about 75% and nickel is added to form in situ precipitation of at least 0.05 wt. % $MgNi_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without nickel additions subjected to the said aging treatment.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the magnesium content is at least about 85% and nickel is added to form in situ precipitation of at least 0.05 wt. % $MgNi_2$ with the magnesium or magnesium alloy and solutionizing

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the resultant metal at a temperature at about 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of nickel.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content in the alloy is at least about 75% and copper is added to form in situ precipitation of at least about 0.05 wt. % MgCu₂ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said aging treatment.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the total content of magnesium in the magnesium or magnesium alloy is at least about 85 wt. % and copper is added to form in situ precipitation of at least 0.05 wt. % MgCu₂ with the magnesium or magnesium composite and solutionizing the resultant metal at a temperature of about 100-500° C. for a period of 0.25-50 hours, the magnesium composite is characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of copper.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable ball or frac ball in hydraulic fracturing and well drilling.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable tool for use in well drilling and hydraulic control as well as hydraulic fracturing.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes secondary institute formed reinforcements that are not galvanically-active to the magnesium or magnesium alloy matrix to increase the mechanical properties of the magnesium composite. The secondary institute formed reinforcements include a Mg₂Si phase as the in situ formed reinforcement.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a faster cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a slower cooling rate from the liquidus to the solidus point to create larger in situ formed particles.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to mechanical agitation during the cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to mechanical agitation during the cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to chemical agitation during the cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

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In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to ultrasonic agitation during the cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to deformation or extrusion to further improve dispersion of the in situ formed particles.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium, b) melting the AZ91 D magnesium alloy to a temperature above 800° C., c) adding up to about 7 wt. % nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 14 ksi, and an elongation of about 3% and a shear strength of 11 ksi. The cast material has a dissolve rate of about 75 mg/cm²-min in a 3% KCl solution at 90° C. The cast material dissolves at a rate of 1 mg/cm²-hr in a 3% KCl solution at 21° C. The cast material dissolves at a rate of 325 mg/cm²-hr. in a 3% KCl solution at 90° C. The cast material can be subjected to extrusion with a 11:1 reduction area. The extruded cast material exhibits a tensile strength of 40 ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm²-min in a 3% KCl solution at 20° C. The extruded cast material dissolves at a rate of 100 mg/cm²-hr. in a 3% KCl solution at 90° C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100° C.-200° C. The aged extruded cast material exhibits a tensile strength of 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi. The aged extruded cast material dissolves at a rate of 110 mg/cm²-hr in 3% KCl solution at 90° C. and 1 mg/cm²-hr in 3% KCl solution at 20° C. The cast material can be subjected to a solutionizing treatment T4 for about 18 hours between 400° C.-500° C. and then subjected to an artificial T6 age treatment for about 16 hours between 100° C.-200° C. The aged and solutionized cast material exhibits a tensile strength of about 34 ksi, an elongation to failure of about 11%, and a shear strength of about 18 ksi. The aged and solutionized cast material dissolves at a rate of about 84 mg/cm²-hr in 3% KCl solution at 90° C., and about 0.8 mg/cm²-hr in 3% KCl solution at 20° C.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800° C., c) adding up to about 1 wt. % nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 18 ksi, and an elongation of about 5% and a shear strength of 17 ksi. The cast material has a dissolve rate of about 45 mg/cm²-min in

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a 3% KCl solution at 90° C. The cast material dissolves at a rate of 0.5 mg/cm²-hr. in a 3% KCl solution at 21° C. The cast material dissolves at a rate of 325 mg/cm²-hr. in a 3% KCl solution at 90° C. The cast material was then subjected to extrusion with a 20:1 reduction area. The extruded cast material exhibits a tensile yield strength of 35 ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm²-min in a 3% KCl solution at 20° C. The extruded cast material dissolves at a rate of 50 mg/cm²-hr in a 3% KCl solution at 90° C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100° C.-200° C. The aged extruded cast material exhibits a tensile strength of 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having about 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800° C., c) adding about 10 wt. % copper to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of copper, d) dispersing the copper in the melted AZ91D magnesium alloy using chemical mixing agents at a temperature that is less than the melting point of copper, and e) cooling casting the melted mixture in a steel mold. The cast material exhibits a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolves at a rate of about 50 mg/cm²-hr. in a 3% KCl solution at 90° C. The cast material dissolves at a rate of 0.6 mg/cm²-hr. in a 3% KCl solution at 21° C. The cast material can be subjected to an artificial T5 age treatment for about 16 hours at a temperature of 100-200° C. The aged cast material exhibits a tensile strength of 50 Ksi, an elongation to failure of 5%, and a shear strength of 25 ksi. The aged cast material dissolved at a rate of 40 mg/cm²-hr in 3% KCl solution at 90° C. and 0.5 mg/cm²-hr in 3% KCl solution at 20° C.

These and other objects, features and advantages of the present invention will become apparent in light of the following detailed description of preferred embodiments thereof, as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-3 show a typical cast microstructure with galvanically-active in situ formed intermetallic phase wetted to the magnesium matrix; and,

FIG. 4 shows a typical phase diagram to create in situ formed particles of an intermetallic Mg_x(M) where M is any element on the periodic table or any compound in a magnesium matrix and wherein M has a melting point that is greater than the melting point of Mg.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a novel magnesium composite that can be used to form a castable, moldable, or extrudable component. The magnesium composite includes at least 50 wt. % magnesium. Generally, the magnesium composite includes over 50 wt. % magnesium and less than about 99.5 wt. % magnesium and all values and ranges therebetween. One or more additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention. The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives are added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are not caused to fully melt in the molten magnesium or magnesium alloy. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or magnesium alloy are cooled to form a solid component. Such a formation in the melt is called in situ particle formation as illustrated in FIGS. 1-3. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the in situ phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The in situ formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the in situ formed particles size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of in situ particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. In situ particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques. A smaller particle size can be used to increase the dissolution rate of the magnesium composite. An increase in the weight percent of the in situ formed particles or phases in the magnesium composite can also or alternatively be used to increase the dissolution rate of the magnesium composite. A phase diagram for forming in situ formed particles or phases in the magnesium composite is illustrated in FIG. 4.

ally-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives are added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are not caused to fully melt in the molten magnesium or magnesium alloy. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or magnesium alloy are cooled to form a solid component. Such a formation in the melt is called in situ particle formation as illustrated in FIGS. 1-3. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the in situ phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The in situ formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the in situ formed particles size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of in situ particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. In situ particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques. A smaller particle size can be used to increase the dissolution rate of the magnesium composite. An increase in the weight percent of the in situ formed particles or phases in the magnesium composite can also or alternatively be used to increase the dissolution rate of the magnesium composite. A phase diagram for forming in situ formed particles or phases in the magnesium composite is illustrated in FIG. 4.

In accordance with the present invention, a novel magnesium composite is produced by casting a magnesium metal or magnesium alloy with at least one component to form a galvanically-active phase with another component in the chemistry that forms a discrete phase that is insoluble at the use temperature of the dissolvable component. The in

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situ formed particles and phases have a different galvanic potential from the remaining magnesium metal or magnesium alloy. The in situ formed particles or phases are uniformly dispersed through the matrix metal or metal alloy using techniques such as thixomolding, stir casting, mechanical agitation, chemical agitation, electrowetting, ultrasonic dispersion, and/or combinations of these methods. Due to the particles being formed in situ to the melt, such particles generally have excellent wetting to the matrix phase and can be found at grain boundaries or as continuous dendritic phases throughout the component depending on alloy composition and the phase diagram. Because the alloys form galvanic intermetallic particles where the intermetallic phase is insoluble to the matrix at use temperatures, once the material is below the solidus temperature, no further dispersing or size control is necessary in the component. This feature also allows for further grain refinement of the final alloy through traditional deformation processing to increase tensile strength, elongation to failure, and other properties in the alloy system that are not achievable without the use of insoluble particle additions. Because the ratio of in situ formed phases in the material is generally constant and the grain boundary to grain surface area is typically consistent even after deformation processing and heat treatment of the composite, the corrosion rate of such composites remains very similar after mechanical processing.

EXAMPLE 1

An AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium was melted to above 800° C. and at least 200° C. below the melting point of nickel. About 7 wt. % of nickel was added to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolved at a rate of about 75 mg/cm²-min in a 3% KCl solution at 90° C. The material dissolved at a rate of 1 mg/cm²-hr in a 3% KCl solution at 21° C. The material dissolved at a rate of 325 mg/cm²-hr. in a 3% KCl solution at 90° C.

EXAMPLE 2

The composite in Example 1 was subjected to extrusion with an 11:1 reduction area. The material exhibited a tensile yield strength of 45 ksi, an Ultimate tensile strength of 50 ksi and an elongation to failure of 8%. The material has a dissolve rate of 0.8 mg/cm²-min. in a 3% KCl solution at 20° C. The material dissolved at a rate of 100 mg/cm²-hr. in a 3% KCl solution at 90° C.

EXAMPLE 3

The alloy in Example 2 was subjected to an artificial T5 age treatment of 16 hours from 100° C.-200° C. The alloy exhibited a tensile strength of 48 ksi and elongation to failure of 5% and a shear strength of 25 ksi. The material dissolved at a rate of 110 mg/cm²-hr. in 3% KCl solution at 90° C. and 1 mg/cm²-hr. in 3% KCl solution at 20° C.

EXAMPLE 4

The alloy in Example 1 was subjected to a solutionizing treatment T4 of 18 hours from 400° C.-500° C. and then an artificial T6 aging treatment of 16 hours from 100° C.-200° C. The alloy exhibited a tensile strength of 34 ksi and

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elongation to failure of 11% and a shear strength of 18 Ksi. The material dissolved at a rate of 84 mg/cm²-hr. in 3% KCl solution at 90° C. and 0.8 mg/cm²-hr. in 3% KCl solution at 20° C.

EXAMPLE 5

An AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium was melted to above 800° C. and at least 200° C. below the melting point of copper. About 10 wt. % of copper alloyed to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile yield strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolved at a rate of about 50 mg/cm²-hr. in a 3% KCl solution at 90° C. The material dissolved at a rate of 0.6 mg/cm²-hr. in a 3% KCl solution at 21° C.

EXAMPLE 6

The alloy in Example 5 was subjected to an artificial T5 aging treatment of 16 hours from 100° C.-200° C. the alloy exhibited a tensile strength of 50 ksi and elongation to failure of 5% and a shear strength of 25 ksi. The material dissolved at a rate of 40 mg/cm²-hr. in 3% KCl solution at 90° C. and 0.5 mg/cm²-hr. in 3% KCl solution at 20° C.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in the constructions set forth without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense. The invention has been described with reference to preferred and alternate embodiments. Modifications and alterations will become apparent to those skilled in the art upon reading and understanding the detailed discussion of the invention provided herein. This invention is intended to include all such modifications and alterations insofar as they come within the scope of the present invention. It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention, which, as a matter of language, might be said to fall there between. The invention has been described with reference to the preferred embodiments. These and other modifications of the preferred embodiments as well as other embodiments of the invention will be obvious from the disclosure herein, whereby the foregoing descriptive matter is to be interpreted merely as illustrative of the invention and not as a limitation. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims.

What is claimed:

1. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material having a greater melting point temperature than a solidus temperature of said magnesium, said additive material constituting about 0.05 wt. %-45 wt. % of said mixture, said additive material forming precipitant in said magnesium composite, said additive material includes one or more metals selected from the group consisting of copper, nickel,

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iron, and cobalt, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

2. The magnesium composite as defined in claim 1, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

3. The magnesium composite as defined in claim 1, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %.

4. The magnesium composite as defined in claim 1, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

5. The magnesium composite as defined in claim 1, wherein said additive material includes copper, said copper constitutes about 0.05-35 wt. % of said magnesium composite, said copper forms galvanically-active in situ precipitate in said magnesium composite.

6. The magnesium composite as defined in claim 1, wherein said additive material includes cobalt, said cobalt constitutes about 0.05-35 wt. % of said magnesium composite, said cobalt forms galvanically-active in situ precipitate in said magnesium composite.

7. The magnesium composite as defined in claim 1, where said magnesium composite is subjected to a deformation processing to reduce grain size of said magnesium composite, increase tensile yield strength of said magnesium composite, increase elongation of said magnesium composite, or combinations thereof.

8. The magnesium composite as defined in claim 1, wherein said magnesium composite is subjected to a surface treatment to improve a surface hardness of said magnesium composite, said surface treatment including peening, heat treatment, aluminizing, or combinations thereof.

9. The magnesium composite as defined in claim 1, wherein a dissolution rate of said magnesium composite is about 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

10. The magnesium composite as defined in claim 1, wherein a dissolution rate of said magnesium composite is controlled by an amount and size of said in situ formed galvanically-active particles whereby smaller average sized particles of said in situ formed galvanically-active particles, a greater weight percent of said in situ formed galvanically-active particles in said magnesium composite, or combinations thereof increases said dissolution rate of said magnesium composite.

11. The magnesium composite as defined in claim 1, wherein said additive material is a metal or metal alloy.

12. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite comprising a mixture of a magnesium or a magnesium alloy and an additive material, said additive material having a greater melting point temperature than a solidus temperature of said magnesium, said composite including greater than 50 wt. % magnesium, said additive material constituting about 0.05-45 wt. % of said magnesium composite, said additive material having a melting point temperature that is 100° C.

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greater than a melting temperature of said magnesium or magnesium alloy, said additive material including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium, and iron, at least a portion of said additive material remaining unalloyed additive material, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that includes said unalloyed additive material, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

13. The magnesium composite as defined in claim 12, wherein said additive material is added to said magnesium or magnesium alloy while said magnesium or magnesium alloy is at a temperature that is above said solidus temperature of said magnesium and a temperature that is less than a melting point of said additive material to form said mixture.

14. The magnesium composite as defined in claim 13, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %.

15. The magnesium composite as defined in claim 14, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

16. The magnesium composite as defined in claim 15, wherein said additive material includes nickel, said nickel constitutes about 3-7 wt. % of said magnesium composite.

17. The magnesium composite as defined in claim 15, wherein said additive material includes nickel, said nickel constitutes about 7-10 wt. % of said magnesium composite.

18. The magnesium composite as defined in claim 15, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

19. The magnesium composite as defined in claim 12, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %.

20. The magnesium composite as defined in claim 12, said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

21. The magnesium composite as defined in claim 20, wherein said additive material includes nickel, said nickel constitutes about 3-7 wt. % of said magnesium composite.

22. The magnesium composite as defined in claim 20, wherein said additive material includes nickel, said nickel constitutes about 7-10 wt. % of said magnesium composite.

23. The magnesium composite as defined in claim 12, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

24. The magnesium composite as defined in claim 12, wherein said additive material is a metal or metal alloy.

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25. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising at least 85 wt. % magnesium; one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

26. The dissolvable magnesium alloy composite as defined in claim 25, wherein a dissolution rate of said magnesium alloy composite is 100-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

27. The dissolvable magnesium composite as defined in claim 25, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

28. The dissolvable magnesium alloy composite as defined in claim 25, wherein said additive material is a metal or metal alloy.

29. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.01-1 wt. % zirconium; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

30. The dissolvable magnesium alloy composite as defined in claim 29, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

31. The dissolvable magnesium composite as defined in claim 29, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

32. The dissolvable magnesium alloy composite as defined in claim 29, wherein said additive material is a metal or metal alloy.

33. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.5-10 wt. % aluminum; 0.05-6 wt. % zinc; 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

34. The dissolvable magnesium alloy composite as defined in claim 33, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

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35. The dissolvable magnesium composite as defined in claim 33, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

36. The dissolvable magnesium alloy composite as defined in claim 33, wherein said additive material is a metal or metal alloy.

37. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising 60-95 wt. % magnesium; 0.05-6 wt. % zinc; 0.01-1 wt. % zirconium; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium and iron, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

38. The dissolvable magnesium alloy composite as defined in claim 37, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

39. The dissolvable magnesium composite as defined in claim 37, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

40. The dissolvable magnesium alloy composite as defined in claim 37, wherein said additive material is a metal or metal alloy.

41. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising over 50 wt. % magnesium; one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel and cobalt, said magnesium alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

42. The dissolvable magnesium alloy composite as defined in claim 41, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

43. The dissolvable magnesium composite as defined in claim 41, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

44. The dissolvable magnesium alloy composite as defined in claim 41, wherein said additive material is a metal or metal alloy.

45. A dissolvable magnesium alloy composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium alloy composite comprising over 50 wt. % magnesium; one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth; and about 0.05-45 wt. % of a secondary metal to form a galvanically-active intermetallic particle that promotes corrosion of said dissolvable magnesium alloy composite, said secondary metal including one or more metals selected from the group consisting of copper, nickel, and cobalt, said magnesium

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alloy composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

46. The dissolvable magnesium alloy composite as defined in claim 45, wherein a dissolution rate of said magnesium alloy composite is 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

47. The dissolvable magnesium composite as defined in claim 45, wherein said secondary metal includes nickel, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

48. The dissolvable magnesium alloy composite as defined in claim 45, wherein said additive material is a metal or metal alloy.

49. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting about 0.05-45 wt. % of said mixture, said additive material includes one or more metals selected from the group consisting of copper, nickel, titanium, iron, and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said additive material located in sufficient quantities in said galvanically-active intermetallic phases so as to obtain a composition and morphology of said galvanically-active intermetallic phases such that a galvanic corrosion rate along said galvanically-active intermetallic phases causes said magnesium composite to have a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

50. The magnesium composite as defined in claim 49, wherein said additive material includes one or more metals selected from the group consisting of copper, nickel, and cobalt.

51. The magnesium composite as defined in claim 49, wherein said additive material includes particles having an average particle diameter size of about 0.1-500 microns.

52. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

53. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in an amount of about 0.1-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in an amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %.

54. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in an amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in an amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %.

55. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes at least 85 wt. % magnesium, and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese.

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56. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes 60-95 wt. % magnesium and 0.01-1 wt. % zirconium.

57. The magnesium composite as defined in claim 56, wherein said magnesium alloy further includes 0.05-6 wt. % zinc.

58. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes 60-95 wt. % magnesium, 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, and 0.15-2 wt. % manganese.

59. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese.

60. The magnesium composite as defined in claim 49, wherein said magnesium alloy includes over 50 wt. % magnesium, and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

61. The magnesium composite as defined in claim 49, wherein said additive material includes nickel, said nickel constitutes about 0.05-35 wt. % of said magnesium composite, said nickel forms galvanically-active in situ precipitate in said magnesium composite.

62. The magnesium composite as defined in claim 61, wherein said nickel constitutes about 3-7 wt. % of said magnesium composite.

63. The magnesium composite as defined in claim 61, wherein said nickel constitutes about 7-10 wt. % of said magnesium composite.

64. The magnesium composite as defined in claim 49, wherein said additive material includes copper, said copper constitutes about 0.05-35 wt. % of said magnesium composite, said copper forms the galvanically-active in situ precipitate in said magnesium composite.

65. The magnesium composite as defined in claim 49, wherein said additive material includes cobalt, said cobalt constitutes about 0.05-35 wt. % of said magnesium composite, said cobalt forms the galvanically-active in situ precipitate in said magnesium composite.

66. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is about 5-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

67. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

68. The magnesium composite as defined in claim 49, wherein a dissolution rate of said magnesium composite is up to 1 mg/cm²/hr. in 3 wt. % KCl water mixture at 21° C.

69. The magnesium composite as defined in claim 49, wherein said additive material has a melting point temperature that is 100° C. greater than a melting temperature of said magnesium or magnesium alloy.

70. The magnesium composite as defined in claim 49, wherein said magnesium composite is at least partially included in a down hole well component, said down hole well component including one or more components selected from the group consisting of a sleeve, frac ball, hydraulic actuating tooling, tube, valve, valve component, or plug.

71. The magnesium composite as defined in claim 49, wherein at least a portion of said additive material remains unalloyed additive material in said magnesium composite.

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72. The magnesium composite as defined in claim 49, wherein said additive material is a metal or metal alloy.

73. A dissolvable magnesium composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium composite includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting about 0.05 wt. % of said mixture, said additive material is a metal or metal alloy, said additive material includes one or more metals selected from the group consisting of copper, nickel, titanium, iron, silicon, and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said additive material located in sufficient quantities in said galvanically-active intermetallic phases so as to obtain a composition and morphology of said galvanically-active intermetallic phases such that a galvanic corrosion rate along said galvanically-active intermetallic phases causes said magnesium composite to have a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

74. A dissolvable magnesium composite for use in a ball or other tool component in a well drilling or completion operation, said dissolvable magnesium composite includes in situ precipitation of galvanically-active intermetallic

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phases to enable controlled dissolution of said magnesium composite, said magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material constituting at least 0.1 wt. % of said mixture, said magnesium in said magnesium composite constituting at least 85 wt. %, said additive material is a metal material selected from the group consisting of copper, nickel and cobalt, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that include said additive material, said magnesium composite has a dissolution rate of 84-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

75. The magnesium composite as defined in claim 74, wherein said magnesium alloy is an AZ91D magnesium alloy that includes aluminum and zinc.

76. The magnesium composite as defined in claim 74, wherein said additive material includes nickel, a content of said nickel in said magnesium composite is at least 0.3 wt. %.

77. The magnesium composite as defined in claim 74, wherein said additive material includes nickel, a content of said nickel in said magnesium composite is at least 7 wt. %.

78. The magnesium composite as defined in claim 74, wherein said additive material includes nickel, a content of said nickel in said magnesium composite is at least 10 wt. %.

* * * * *

(12) **United States Patent**
Doud et al.

(10) **Patent No.:** **US 10,689,740 B2**

(45) **Date of Patent:** ***Jun. 23, 2020**

(54) **GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS**

(58) **Field of Classification Search**

CPC ... C22F 1/06; C22C 23/02; C22C 1/02; C22C 23/00

See application file for complete search history.

(71) Applicant: **Terves Inc.**, Euclid, OH (US)

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ABSTRACT

A castable, moldable, and/or extrudable structure using a metallic primary alloy. One or more additives are added to the metallic primary alloy so that in situ galvanically-active reinforcement particles are formed in the melt or on cooling from the melt. The composite contains an optimal composition and morphology to achieve a specific galvanic corrosion rate in the entire composite. The in situ formed galvanically-active particles can be used to enhance mechanical properties of the composite, such as ductility and/or tensile strength. The final casting can also be enhanced by heat treatment, as well as deformation processing such as extrusion, forging, or rolling, to further improve the strength of the final composite over the as-cast material.

103 Claims, 3 Drawing Sheets

(65) **Prior Publication Data**

US 2019/0048448 A1 Feb. 14, 2019

Related U.S. Application Data

(60) Continuation-in-part of application No. 15/641,439, filed on Jul. 5, 2017, now Pat. No. 10,329,653, which
(Continued)

(51) **Int. Cl.**

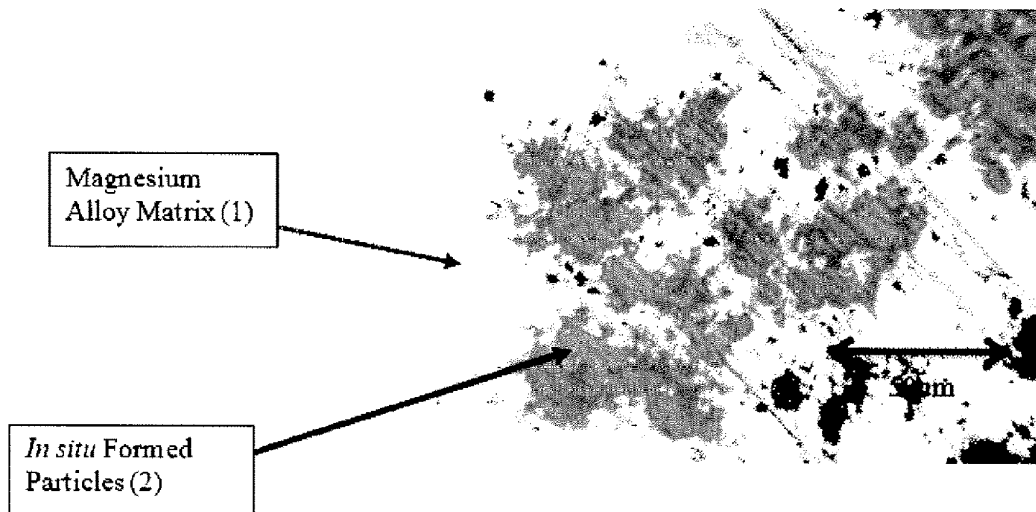
C22F 1/06 (2006.01)

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(Continued)

(52) **U.S. Cl.**

CPC **C22F 1/06** (2013.01); **C22C 1/02** (2013.01); **C22C 23/00** (2013.01); **C22C 23/02** (2013.01)



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is a division of application No. 14/689,295, filed on Apr. 17, 2015, now Pat. No. 9,903,010.

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(51) **Int. Cl.**

C22C 23/00 (2006.01)

C22C 1/02 (2006.01)

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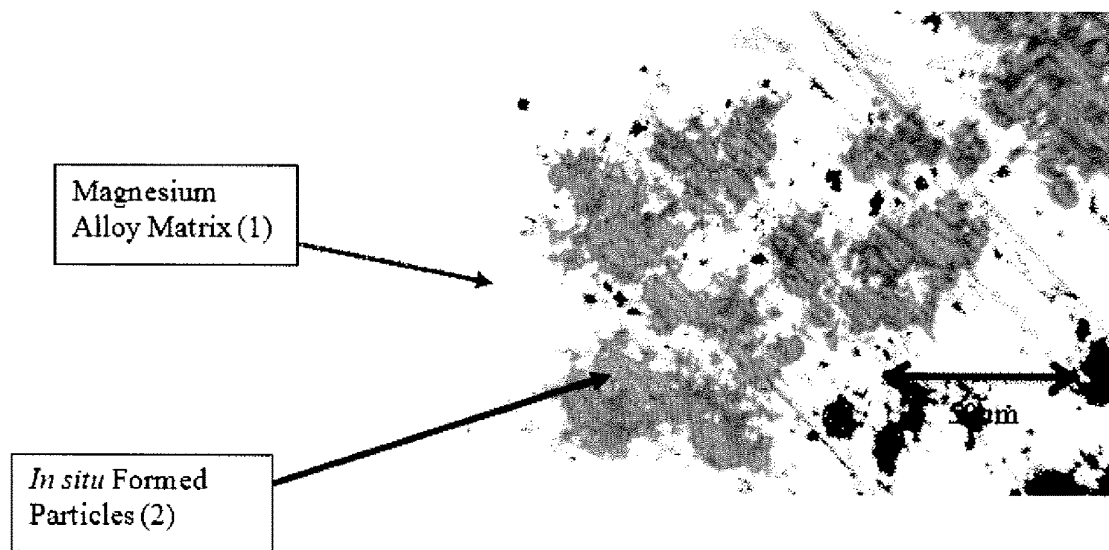


FIG. 1

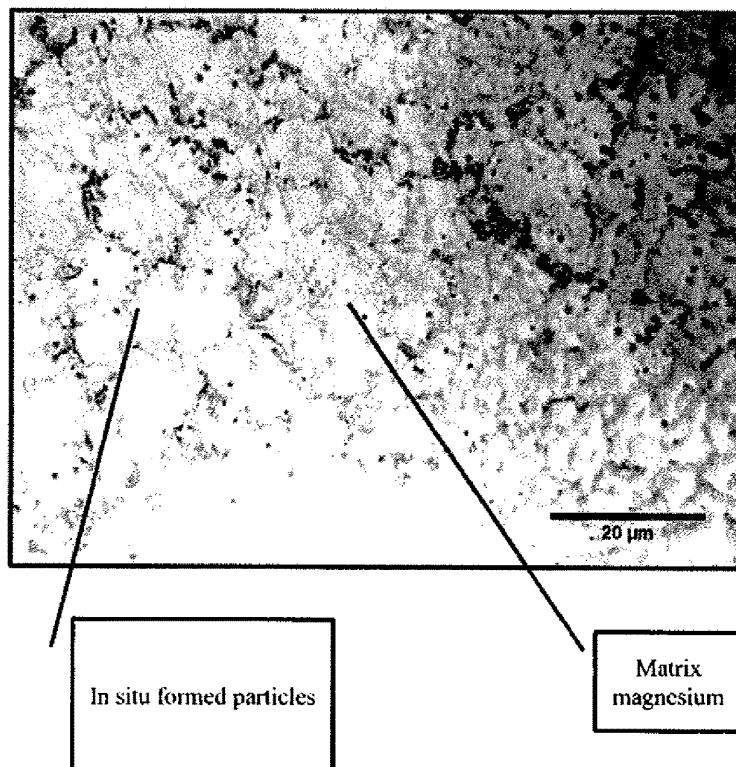
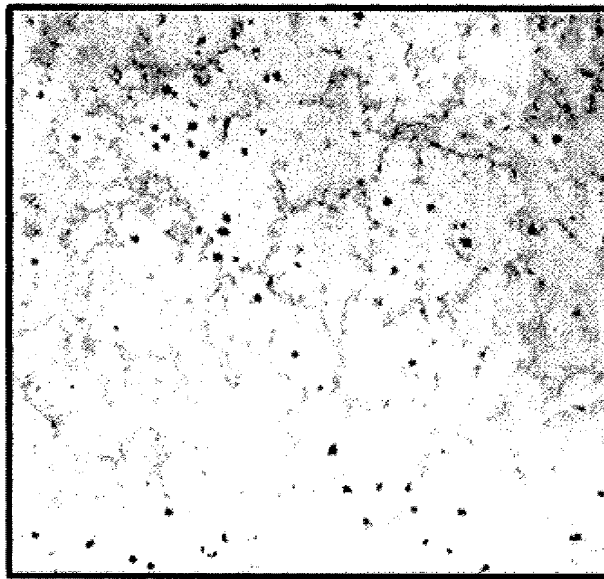


FIG. 2



Highlighted In Situ Formed Particles

FIG. 3

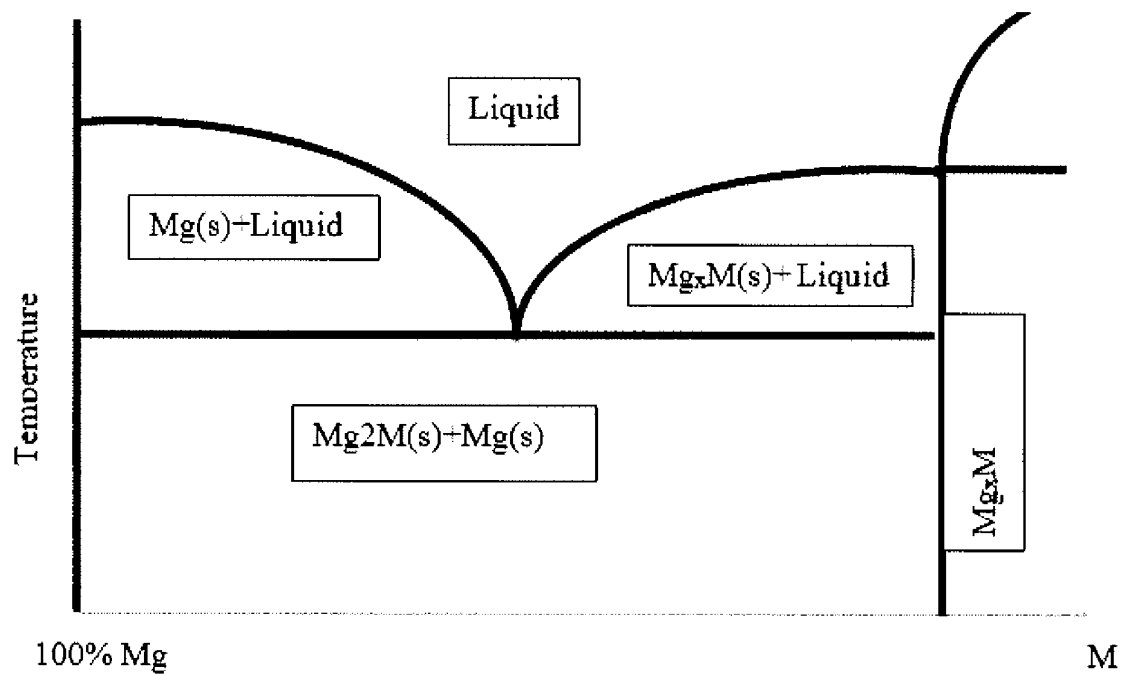


FIG. 4

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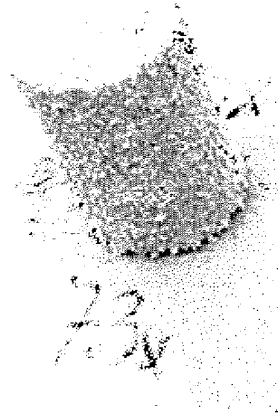


FIG. 5

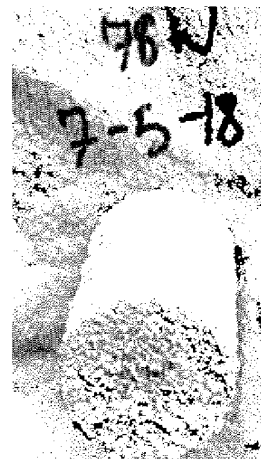
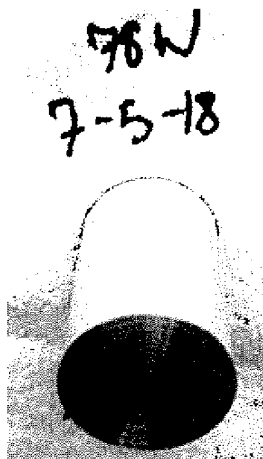


FIG. 6

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GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS

The present invention is a continuation-in-part of U.S. patent application Ser. No. 15/641,439 filed Jul. 5, 2017, which in turn is a divisional of U.S. patent application Ser. No. 14/689,295 filed Apr. 17, 2015 (now U.S. Pat. No. 9,903,010 issued Feb. 27, 2018), which in turn claims priority on U.S. Provisional Patent Application Ser. No. 61/981,425 filed Apr. 18, 2014, which are incorporated herein by reference.

FIELD OF THE INVENTION

The present invention is directed to a novel magnesium composite for use as a dissolvable component in oil drilling. The invention is also directed to a novel material for use as a dissolvable structure in oil drilling. Specifically, the invention is directed to a ball or other structure in a well drilling or completion operation, such as a structure that is seated in a hydraulic operation, that can be dissolved away after use so that that no drilling or removal of the structure is necessary. Primarily, dissolution is measured as the time the ball removes itself from the seat or can become free floating in the system. Secondly, dissolution is measured in the time the ball is substantially or fully dissolved into submicron particles. Furthermore, the novel material of the present invention can be used in other well structures that also desire the function of dissolving after a period of time. The material is machinable and can be used in place of existing metallic or plastic structures in oil and gas drilling rigs including, but not limited to, water injection and hydraulic fracturing.

BACKGROUND OF THE INVENTION

The ability to control the dissolution of a downhole well component in a variety of solutions is important to the utilization of non-drillable completion tools, such as sleeves, frac balls, hydraulic actuating tooling, and the like. Reactive materials for this application, which dissolve or corrode when exposed to acid, salt, and/or other wellbore conditions, have been proposed for some time. Generally, these components consist of materials that are engineered to dissolve or corrode.

While the prior art well drill components have enjoyed modest success in reducing well completion costs, their consistency and ability to specifically control dissolution rates in specific solutions, as well as other drawbacks such as limited strength and poor reliability, have impacted their widespread adoption. Ideally, these components would be manufactured by a process that is low cost, scalable, and produces a controlled corrosion rate having similar or increased strength as compared to traditional engineering alloys such as aluminum, magnesium, and iron. Ideally, traditional heat treatments, deformation processing, and machining techniques could be used on the components without impacting the dissolution rate and reliability of such components.

Prior art articles regarding calcium use in magnesium are set for in Koltygin et al., "Effect of calcium on the process of production and structure of magnesium melted by flux-free method" *Magnesium and Its Alloys* (2013): 540-544; Koltygin et al., "Development of a magnesium alloy with good casting characteristics on the basis of Mg—Al—Ca—Mn system, having Mg—Al₂Ca structure." *Journal of Magnesium and Alloys* 1 (2013): 224-229; Li et al., "Develop-

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ment of non-flammable high strength AZ91+Ca alloys via liquid forging and extrusion." *Materials and Design* (2016): 37-43; Cheng et al. "Effect of Ca and Y additions on oxidation behavior of AZ91 alloy at elevated temperatures." *Transactions of Nonferrous Metals Society of China* (2009): 299-304; and Qudong et al., "Effects of Ca addition on the microstructure and mechanical properties of AZ91 magnesium alloy." *Journal of Materials Science* (2001): 3035-3040.

SUMMARY OF THE INVENTION

The present invention is directed to a novel magnesium composite for use as a dissolvable component in oil drilling and will be described with particular reference to such application. As can be appreciated, the novel magnesium composite of the present invention can be used in other applications (e.g., non-oil wells, etc.). In one non-limiting embodiment, the present invention is directed to a ball or other tool component in a well drilling or completion operation such as, but not limited to, a component that is seated in a hydraulic operation that can be dissolved away after use so that no drilling or removal of the component is necessary. Tubes, valves, valve components, plugs, frac balls, sleeve, hydraulic actuating tooling, mandrels, slips, grips, balls, darts, carriers, valve components, other downhole well components and other shapes of components can also be formed of the novel magnesium composite of the present invention. For purposes of this invention, primary dissolution is measured for valve components and plugs as the time the part removes itself from the seat of a valve or plug arrangement or can become free floating in the system. For example, when the part is a plug in a plug system, primary dissolution occurs when the plug has degraded or dissolved to a point that it can no longer function as a plug and thereby allows fluid to flow about the plug. For purposes of this invention, secondary dissolution is measured in the time the part is fully dissolved into submicron particles. As can be appreciated, the novel magnesium composite of the present invention can be used in other well components that also desire the function of dissolving after a period of time. In one non-limiting aspect of the present invention, a galvanically-active phase is precipitated from the novel magnesium composite composition and is used to control the dissolution rate of the component; however, this is not required. The novel magnesium composite is generally castable and/or machinable and can be used in place of existing metallic or plastic components in oil and gas drilling rigs including, but not limited to, water injection and hydraulic fracturing. The novel magnesium composite can be heat treated as well as extruded and/or forged.

In one non-limiting aspect of the present invention, the novel magnesium composite is used to form a castable, moldable, or extrudable component. Non-limiting magnesium composites in accordance with the present invention include at least 50 wt. % magnesium. One or more additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention. The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives can be in the form of a pure or nearly pure additive element (e.g., at least 98% pure), or can be added as an alloy of two or more additive elements or an alloy of magnesium and one or more additive elements. The

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one or more additives typically are added in a weight percent that is less than a weight percent of said magnesium or magnesium alloy. Typically, the magnesium or magnesium alloy constitutes about 50.1-99.9 wt. % of the magnesium composite and all values and ranges therebetween. In one non-limiting aspect of the invention, the magnesium or magnesium alloy constitutes about 60-95 wt. % of the magnesium composite, and typically the magnesium or magnesium alloy constitutes about 70-90 wt. % of the magnesium composite. The one or more additives can be added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives; however, this is not required. The one or more additives generally have an average particle diameter size of at least about 0.1 microns, typically no more than about 500 microns (e.g., 0.1 microns, 0.1001 microns, 0.1002 microns . . . 499.9998 microns, 499.9999 microns, 500 microns) and include any value or range therebetween, more typically about 0.1-400 microns, and still more typically about 10-50 microns. In one non-limiting configuration, the particles can be less than 1 micron. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives do not typically fully melt in the molten magnesium or magnesium alloy; however, the one or more additives can form a single-phase liquid with the magnesium while the mixture is in the molten state. As can be appreciated, the one or more additives can be added to the molten magnesium or magnesium alloy at a temperature that is greater than the melting point of the one or more additives. The one or more additives can be added individually as pure or substantially pure additive elements or can be added as an alloy that is formed of a plurality of additive elements and/or an alloy that includes one or more additive elements and magnesium. When one or more additive elements are added as an alloy, the melting point of the alloy may be less than the melting point of one or more of the additive elements that are used to form the alloy; however, this is not required. As such, the addition of an alloy of the one or more additive elements could be caused to melt when added to the molten magnesium at a certain temperature, whereas if the same additive elements were individually added to the molten magnesium at the same temperature, such individual additive elements would not fully melt in the molten magnesium.

The one or more additives are selected such that as the molten magnesium cools, newly formed metallic alloys and/or additives begin to precipitate out of the molten metal and form the in situ phase to the matrix phase in the cooled and solid magnesium composite. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or magnesium alloy are cooled to form a solid component. In one non-limiting embodiment, the temperature of the molten magnesium or magnesium alloy is at least about 10° C. less than the melting point of the additive that is added to the molten magnesium or magnesium alloy during the addition and mixing process, typically at least about 100° C. less than the melting point of the additive that is added to the molten magnesium or magnesium alloy during the addition and mixing process, more typically about 100-1000° C. (and any value or range therebetween) less than the melting point of the additive that is added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required. As can be appreciated, one or more additives in the form of an alloy or a pure or substantially pure additive element can be added to the magnesium that have a melting point that is less than the

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melting point of magnesium, but still at least partially precipitate out of the magnesium as the magnesium cools from its molten state to a solid state. Generally, such one or more additives and/or one or more components of the additives form an alloy with the magnesium and/or one or more other additives in the molten magnesium. The formed alloy has a melting point that is greater than a melting point of magnesium, thereby results in the precipitation of such formed alloy during the cooling of the magnesium from the molten state to the solid state. The never melted additive(s) and/or the newly formed alloys that include one or more additives are referred to as in situ particle formation in the molten magnesium composite. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite.

The invention adopts a feature that is usually a negative in traditional casting practices wherein a particle is formed during the melt processing that corrodes the alloy when exposed to conductive fluids and is imbedded in eutectic phases, the grain boundaries, and/or even within grains with precipitation hardening. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the in situ phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The in situ formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the in situ formed particle size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of in situ particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. In situ particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques.

In another non-limiting aspect of the invention, a cast structure can be made into almost any shape. During formation, the active galvanically-active in situ phases can be uniformly dispersed throughout the component and the grain or the grain boundary composition can be modified to achieve the desired dissolution rate. The galvanic corrosion can be engineered to affect only the grain boundaries and/or can affect the grains as well (based on composition); however, this is not required. This feature can be used to enable

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fast dissolutions of high-strength lightweight alloy composites with significantly less active (cathode) in situ phases as compared to other processes.

In still another and/or alternative non-limiting aspect of the invention, ultrasonic processing can be used to control the size of the in situ formed galvanically-active phases; however, this is not required. Ultrasonic energy is used to degass and grain refine alloys, particularly when applied in the solidification region. Ultrasonic and stirring can be used to refine the grain size in the alloy, thereby creating a high strength alloy and also reducing dispersoid size and creating more equiaxed (uniform) grains. Finer grains in the alloy have been found to reduce the degradation rate with equal amounts of additives.

In yet another and/or alternative non-limiting aspect of the invention, the in situ formed particles can act as matrix strengtheners to further increase the tensile strength of the material compared to the base alloy without the one or more additives; however, this is not required. For example, tin can be added to form a nanoscale precipitate (can be heat treated, e.g., solutionized and then precipitated to form precipitates inside the primary magnesium grains). The particles can be used to increase the strength of the alloy by at least 10%, and as much as greater than 100%, depending on other strengthening mechanisms (second phase, grain refinement, solid solution) strengthening present.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method of controlling the dissolution properties of a metal selected from the class of magnesium and/or magnesium alloy comprising of the steps of a) melting the magnesium or magnesium alloy to a point above its solidus, b) introducing one or more additives to the magnesium or magnesium alloy in order to achieve in situ precipitation of galvanically-active intermetallic phases, and c) cooling the melt to a solid form. The one or more additives are generally added to the magnesium or magnesium alloy when the magnesium or magnesium alloy is in a molten state and at a temperature that is less than the melting point of one or more additive materials. As can be appreciated, one or more additives can be added to the molten magnesium or magnesium alloy at a temperature that is greater than the melting point of the one or more additives. The one or more additives can be added as individual additive elements to the magnesium or magnesium alloy, or be added in alloy form as an alloy of two or more additives, or an alloy of one or more additives and magnesium or magnesium alloy. The galvanically-active intermetallic phases can be used to enhance the yield strength of the alloy; however, this is not required. The size of the in situ precipitated intermetallic phase can be controlled by a melt mixing technique and/or cooling rate; however, this is not required. It has been found that the addition of the one or more additives (SM) to the molten magnesium or magnesium alloy can result in the formation of $MgSM_x$, $MgxSM$, and LPSO and other phases with two, three, or even four components that include one or more galvanically-active additives that result in the controlled degradation of the formed magnesium composite when exposed to certain environments (e.g., salt water, brine, fracking liquids, etc.). The method can include the additional step of subjecting the magnesium composite to intermetallic precipitates to solutionizing of at least about 300° C. to improve tensile strength and/or improve ductility; however, this is not required. The solutionizing temperature is less than the melting point of the magnesium composite. Generally, the solutionizing temperature is less than 50-200° C. of the melting point of the magnesium composite and the time period of solutionizing

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is at least 0.1 hours. In one non-limiting aspect of the invention, the magnesium composite can be subjected to a solutionizing temperature for about 0.5-50 hours (and all values and ranges therebetween) (e.g., 1-15 hours, etc.) at a temperature of 300-620° C. (and all values and ranges therebetween) (e.g., 300-500° C., etc.). The method can include the additional step of subjecting the magnesium composite to intermetallic precipitates and to artificially age the magnesium composite at a temperature at least about 90° C. to improve the tensile strength; however, this is not required. The artificial aging process temperature is typically less than the solutionizing temperature and the time period of the artificial aging process temperature is typically at least 0.1 hours. Generally, the artificial aging process at is less than 50-400° C. (the solutionizing temperature). In one non-limiting aspect of the invention, the magnesium composite can be subjected to the artificial aging process for about 0.5-50 hours (and all values and ranges therebetween) (e.g., 1-16 hours, etc.) at a temperature of 90-300° C. (and all values and ranges therebetween) (e.g., 100-200° C.).

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.5-49.5 wt. % of additive (SM) (e.g., aluminum, zinc, tin, beryllium, boron carbide, copper, nickel, bismuth, cobalt, titanium, manganese, potassium, sodium, antimony, indium, strontium, barium, silicon, lithium, silver, gold, cesium, gallium, calcium, iron, lead, mercury, arsenic, rare earth metals (e.g., yttrium, lanthanum, samarium, europium, gadolinium, terbium, dysprosium, holmium, ytterbium, etc.) and zirconium) (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle. The one or more additives can be added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than or greater than the melting point of the one or more additives. In one non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be less than the melting point of the one or more additives.

In another non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be greater than the melting point of the one or more additives.

In another non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be greater than the melting point of the one or more additives and less than the melting point of one or more other additives.

In another non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be greater than the melting point of the alloy that includes one or more additives.

In another non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be less than the melting point of the alloy that includes one or more additives. During the mixing process, solid particles of $SMMg_x$, SM_xMg can be formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, $SMMg_x$, SM_xMg , and/or any unalloyed additive is cooled and an in situ precipitate is formed in the solid magnesium composite.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-49.5 wt. % nickel (and all values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic Mg_2Ni

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as a galvanically-active in situ precipitate. In one non-limiting arrangement, the magnesium composite includes about 0.05-23.5 wt. % nickel, 0.01-5 wt. % nickel, 3-7 wt. % nickel, 7-10 wt. % nickel, or 10-24.5 wt. % nickel. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel; however, this is not required. In one non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni can be formed; but is not required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, any solid particles of Mg_2Ni , and any unalloyed nickel particles are cooled and an in situ precipitate of any solid particles of Mg_2Ni and any unalloyed nickel particles is formed in the solid magnesium composite. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-49.5 wt. % copper (and all values or ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically-active in situ precipitate that includes copper and/or copper alloy. In one non-limiting arrangement, the magnesium composite includes about 0.01-5 wt. % copper, about 0.5-15 wt. % copper, about 15-35 wt. % copper, or about 0.01-20 wt. % copper. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper; however, this is not required. In one non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper; however, this is not required. During the mixing process, solid particles of $CuMg_2$ can be formed; but is not required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, any solid particles of $CuMg_2$, and any unalloyed copper particles are cooled and an in situ precipitate of any solid particles of $CuMg_2$ and any unalloyed copper particles is formed in the solid magnesium composite. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the copper added to the molten magnesium or magnesium alloy; however, this is not required.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-49.5% by weight cobalt (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically active in situ precipitate that includes cobalt and/or cobalt alloy. In one non-limiting arrangement, the magnesium composite includes about 0.01-5 wt. % cobalt, about 0.5-15 wt. % cobalt, about 15-35 wt. % cobalt, or about 0.01-20 wt. % cobalt. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt; however, this is not required. In one non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt; however, this is not required. During the mixing process, solid particles of $CoMg_2$ and/or Mg_xCo can be formed; but is not

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required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, any solid particles of $CoMg_2$, Mg_xCo , any solid particles of any unalloyed cobalt particles are cooled and an in situ precipitate of any solid particles of $CoMg_2$, Mg_xCo , any solid particles of unalloyed cobalt particles is formed in the solid magnesium composite. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the cobalt added to the molten magnesium or magnesium alloy; however, this is not required.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and up to about 49.5% by weight bismuth (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically-active in situ precipitate that includes bismuth and/or bismuth alloy. Bismuth intermetallics are formed above roughly 0.1 wt. % bismuth, and bismuth is typically useful up to its eutectic point of roughly 11 wt. % bismuth. Beyond the eutectic point, a bismuth intermetallic is formed in the melt. This is typical of additions, in that the magnesium-rich side of the eutectic forms flowable, tastable materials with active precipitates or intermetallics formed at the solidus (in the eutectic mixture), rather than being the primary, or initial, phase solidified. In desirable alloy formulations, alpha magnesium (may be in solid solution with alloying elements) should be the initial/primary phase formed upon initial cooling. In one non-limiting embodiment, bismuth is added to the magnesium composite at an amount of greater than 11 wt. %, and typically about 11.1-30 wt. % (and all values and ranges therebetween).

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and up to about 49.5% by weight tin (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically-active in situ precipitate that includes tin and/or tin alloy. Tin additions have a significant solubility in solid magnesium at elevated temperatures, forming both a eutectic (at grain boundaries), as well as in the primary magnesium (dispersed). Dispersed precipitates, which can be controlled by heat treatment, lead to large strengthening, while eutectic phases are particularly effective at initiating accelerated corrosion rates. In one non-limiting embodiment, tin is added to the magnesium composite at an amount of at least 0.5 wt. %, typically about 1-30 wt. % (and all values and ranges therebetween), and more typically about 1-10 wt. %.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and up to about 49.5% by weight gallium (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically active in situ precipitate that includes gallium and/or gallium alloy. Gallium additions are particularly effective at initiating accelerated corrosion, in concentrations that form up to 3-5 wt. % Mg_3Ga_2 . Gallium alloys are heat treatable forming corrodible high strength alloys. Gallium is fairly unique, in that it has high solubility in solid magnesium, and forms highly corrosive particles during solidification which are located inside the primary magnesium (when below the solid solubility limit), such that both grain boundary and primary (strengthening precipitates) are formed in the magnesium-gallium systems and also in magnesium-indium systems. At gallium concentrations of less than about 3 wt. %, additional superheat (higher melt temperatures) is typically used to form the precipitate in the magnesium alloy. To place

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Mg₅Ga₂ particles at the grain boundaries, gallium concentrations above the solid solubility limit at the pouring temperature are used such that Mg₅Ga₂ phase is formed from the eutectic liquid. In one non-limiting embodiment, gallium is added to the magnesium composite at an amount of at least 1 wt. %, and typically about 1-10 wt. % (and all values and ranges therebetween), typically 2-8 wt. %, and more typically 3.01-5 wt. %.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and up to about 49.5% by weight indium (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically-active in situ precipitate that includes indium and/or indium alloy. Indium additions have also been found effective at initiating corrosion. In one non-limiting embodiment, indium is added to the magnesium composite at an amount of at least 1 wt. %, and typically about 1-30 wt. % (and all values and ranges therebetween).

In general, precipitates having an electronegativity greater than 1.4-1.5 act as corrosion acceleration points, and are more effective if formed from the eutectic liquid during solidification, than precipitation from a solid solution. Alloying additions added below their solid solubility limit which precipitate in the primary magnesium phase during solidification (as opposed to long grain boundaries), and which can be solutionized are more effective in creating higher strength, particularly in as-cast alloys.

In another and/or alternative non-limiting aspect of the invention, the molten magnesium or magnesium alloy that includes the one or more additives can be controllably cooled to form the in situ precipitate in the solid magnesium composite. In one non-limiting embodiment, the molten magnesium or magnesium alloy that includes the one or more additives is cooled at a rate of greater than 1° C. per minute. In one non-limiting embodiment, the molten magnesium or magnesium alloy that includes the one or more additives is cooled at a rate of less than 1° C. per minute. In one non-limiting embodiment, the molten magnesium or magnesium alloy that includes the one or more additives is cooled at a rate of greater than 0.01° C. per min and slower than 1° C. per minute. In one non-limiting embodiment, the molten magnesium or magnesium alloy that includes the one or more additives is cooled at a rate of greater than 10° C. per minute and less than 100° C. per minute. In one non-limiting embodiment, the molten magnesium or magnesium alloy that includes the one or more additives is cooled at a rate of less than 10° C. per minute.

In another non-limiting embodiment, the molten magnesium or magnesium alloy that includes the one or more additives is cooled at a rate 10-100° C./min (and all values and ranges therebetween) through the solidus temperature of the alloy to form fine grains in the alloy.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium alloy that includes over 50 wt. % magnesium (e.g., 50.01-99.99 wt. % and all values and ranges therebetween) and includes at least one metal selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese. As can be appreciated, the magnesium alloy can include one or more additional metals. In one non-limiting embodiment, the magnesium alloy includes over 50 wt. % magnesium and includes at least one metal selected from the group consisting of aluminum in an amount of about 0.05-10 wt. % (and all values and ranges therebetween), zinc in amount of about 0.05-6 wt. % (and all values and ranges therebetween), zirconium in an amount of about 0.01-3 wt. % (and all

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values and ranges therebetween), and/or manganese in an amount of about 0.015-2 wt. % (and all values and ranges therebetween).

In another non-limiting formulation, the magnesium alloy includes over 50 wt. % magnesium and includes at least one metal selected from the group consisting of zinc in amount of about 0.05-6 wt. %, zirconium in an amount of about 0.05-3 wt. %, manganese in an amount of about 0.05-0.25 wt. %, boron (optionally) in an amount of about 0.0002-0.04 wt. %, and bismuth (optionally) in an amount of about 0.4-0.7 wt. %. In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium alloy that is over 50 wt. % magnesium and at least one metal selected from the group consisting of aluminum in an amount of about 0.05-10 wt. % (and all values and ranges therebetween), zinc in an amount of about 0.05-6 wt. % (and all values and ranges therebetween), calcium in an amount of about 0.5-8 wt. % (and all values and ranges therebetween), zirconium in amount of about 0.05-3 wt. % (and all values and ranges therebetween), manganese in an amount of about 0.05-0.25 wt. % (and all values and ranges therebetween), boron in an amount of about 0.0002-0.04 wt. % (and all values and ranges therebetween), and/or bismuth in an amount of about 0.04-0.7 wt. % (and all values and ranges therebetween).

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium to which nickel in an amount of about 10-24.5 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. Partially or throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be less than the melting point of the nickel; however, this is not required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of alloyed nickel and any unalloyed nickel particles form an in situ precipitate of solid particles in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium to which copper in an amount of about 0.01-5 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. Partially or throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be less than the melting point of the copper; however, this is not required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of copper alloy and any unalloyed copper particles form an in situ precipitate in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium to which copper in an amount of about 0.5-15 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. Partially or

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throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be less than the melting point of the copper; however, this is not required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of copper alloy and any unalloyed copper particles form an in situ precipitate in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium to which copper in an amount of about 15-35 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. Partially or throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be less than the melting point of the copper; however, this is not required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of copper alloy and any unalloyed copper particles form an in situ precipitate in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium to which copper in an amount of about 0.01-20 wt. % is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. Partially or throughout the mixing process, the temperature of the molten magnesium or magnesium alloy can be less than the melting point of the copper; however, this is not required. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of copper alloy and any unalloyed copper particles form an in situ precipitate in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is not required.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and about 0.05-49.5% by weight cobalt (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically active in situ precipitate that includes cobalt and/or cobalt alloy. In one non-limiting arrangement, the magnesium composite includes about 0.01-5 wt. % cobalt, about 0.5-15 wt. % cobalt, about 15-35 wt. % cobalt, or about 0.01-20 wt. % cobalt. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt; however, this is not required. In one non-limiting embodiment, throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt; however, this is not required. During the mixing process, solid particles of CoMg_2 and/or Mg_2Co can be formed; but is not required. Once the mixing process is complete, the mixture of molten

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magnesium or magnesium alloy, any solid particles of CoMg_2 , Mg_2Co , any solid particles of any unalloyed cobalt particles are cooled and an in situ precipitate of any solid particles of CoMg_2 , Mg_2Co , any solid particles of unalloyed cobalt particles is formed in the solid magnesium composite. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200° C. less than the melting point of the cobalt added to the molten magnesium or magnesium alloy; however, this is not required.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium to which bismuth in an amount of about 49.5 wt. % (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically-active in situ precipitate that includes bismuth and/or bismuth alloy. Bismuth intermetallics are formed at above roughly 0.1 wt. % intermetallic is formed in the melt. This is typical of additions, in that the magnesium-rich side of the eutectic forms flowable, castable materials with active precipitates or intermetallics formed at the solidus (in the eutectic mixture), rather than being the primary, or initial, phase solidified. In desirable alloy formulations, alpha magnesium (may be in solid solution with alloying elements) should be the initial/primary phase formed upon initial cooling. In one non-limiting embodiment, bismuth is added to the magnesium composite at an amount of greater than 11 wt. %, and typically about 11.1-30 wt. % and all values and ranges therebetween).

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and up to about 49.5% by weight tin (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically-active in situ precipitate that includes tin and/or tin alloy. Tin additions have a significant solubility in solid magnesium at elevated temperatures, forming both a eutectic (at grain boundaries), as well as in the primary magnesium (dispersed). Dispersed precipitates, which can be controlled by heat treatment, lead to large strengthening, while eutectic phases are particularly effective at initiating accelerated corrosion rates. In one non-limiting embodiment, tin is added to the magnesium composite at an amount of at least 0.5 wt. %, typically about 1-30 wt. % (and all values and ranges therebetween), and more typically about 1-10 wt. %.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and up to about 49.5% by weight gallium (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically active in situ precipitate that includes gallium and/or gallium alloy. Gallium additions are particularly effective at initiating accelerated corrosion, in concentrations that form up to 3-5 wt. % Mg_3Ga_2 . Gallium alloys are heat treatable forming corrodible high strength alloys. Gallium is fairly unique, in that it has high solubility in solid magnesium, and forms highly corrosive particles during solidification which are located inside the primary magnesium (when below the solid solubility limit), such that both grain boundary and primary (strengthening precipitates) are formed in the magnesium-gallium systems and also in magnesium-indium systems. At gallium concentrations of less than about 3 wt. %, additional superheat (higher melt temperatures) is typically used to form the precipitate in the magnesium alloy. To place Mg_3Ga_2 particles at the grain boundaries, gallium concentrations above the solid solubility limit at the pouring temperature are used such that Mg_3Ga_2 phase is formed from the eutectic liquid. In one non-limiting embodiment,

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gallium is added to the magnesium composite at an amount of at least 1 wt. %, and typically about 1-10 wt. % (and all values and ranges therebetween), typically 2-8 wt. %, and more typically 3.01-5 wt. %.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium to which indium in an amount of up to about 49.5 wt. % (and all values and ranges therebetween) is added to the magnesium or magnesium alloy to form galvanically-active in situ precipitate that includes gallium and/or gallium alloy.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and includes one or more additives that have an electronegativity that is greater than 1.5, and typically greater than 1.75, and more typically greater than 1.8. It has been found that by adding such one or more additives to a molten magnesium or molten magnesium alloy, galvanically-active phases can be formed in the solid magnesium composite having desired dissolution rates in salt water, fracking liquid or brine environments. The one or more additives are added to the molten magnesium or molten magnesium alloy such that the final magnesium composite includes 0.05-49.55% by weight of the one or more additives (and all values and ranges therebetween), and typically 0.5-35% by weight of the one or more additives. The one or more additives having an electronegativity that is greater than 1.5 and have been found to form galvanically-active phases in the solid magnesium composite to enhance the dissolution rate of the magnesium composite in salt water, fracking liquid or brine environments are tin, nickel, iron, cobalt, silicon, nickel, chromium, copper, bismuth, lead, tin, antimony, indium, silver, aluminum, gold, platinum, cadmium, selenium, arsenic, boron, germanium, carbon, molybdenum, tungsten, manganese, zinc, rhenium, and gallium. The magnesium composite can include only one of these additives or a plurality of these additives.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt. % magnesium and includes one or more additives in the form of a first additive that has an electronegativity that is 1.5 or greater, and typically greater than 1.8. The electronegativity of magnesium is 1.31. As such, the first additive has a higher electronegativity than magnesium. The first additive can include one or more metals selected from the group consisting of tin (1.96), nickel (1.91), iron (1.83), cobalt (1.88), silicon (1.9), nickel (1.91), copper (1.9), bismuth (2.02), lead (2.33), tin (1.96), antimony (2.05), indium (1.78), silver (1.93), gold (2.54), platinum (2.28), selenium (2.55), arsenic (2.18), boron (2.04), germanium (2.01), carbon (2.55), molybdenum (2.16), tungsten (2.36), chromium (1.66), rhenium (1.9), aluminum (1.61), cadmium (1.68), zinc (1.65), manganese (1.55), and gallium (1.81). As can be appreciated, other or additional metals having an electronegativity of 1.5 or greater can be used.

It has been found that by adding one or more first additives to a molten magnesium or molten magnesium alloy, galvanically-active phases can be formed in the solid magnesium composite having desired dissolution rates in salt water, fracking liquid or brine environments. The one or more first additives are added to the molten magnesium or molten magnesium alloy such that the final magnesium composite includes 0.05-49.55% by weight of the one or more first additives (and all values and ranges therebetween), and typically 0.5-35% by weight of the one or more

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first additives. The one or more first additives having an electronegativity that is greater than 1.5 have been found to form galvanically-active phases in the solid magnesium composite to enhance the dissolution rate of the magnesium composite in salt water, fracking liquid or brine environments.

In yet another and/or alternative non-limiting aspect of the invention, it has been found that in addition to the adding of one or more first additives having an electronegativity that is greater than 1.5 to the molten magnesium or molten magnesium alloy to enhance the dissolution rates of the magnesium composite in salt water, fracking liquid or brine environments, one or more second additives that have an electronegativity of 1.25 or less can also be added to the molten magnesium or molten magnesium alloy to further enhance the dissolution rates of the solid magnesium composite. The one or more second additives can optionally be added to the molten magnesium or molten magnesium alloy such that the final magnesium composite includes 0.05-35% by weight of the one or more second additives (and all values and ranges therebetween), and typically 0.5-30% by weight of the one or more second additives. The second additive can include one or more metals selected from the group consisting of calcium (1.0), strontium (0.95), barium (0.89), potassium (0.82), neodymium (1.14), cerium (1.12), sodium (0.93), lithium (0.98), cesium (0.79), and the rare earth metals such as yttrium (1.22), lanthanum (1.1), samarium (1.17), europium (1.2), gadolinium (1.2), terbium (1.1), dysprosium (1.22), holmium (1.23), and ytterbium (1.1). As can be appreciated, other or additional metals having an electronegativity of 1.25 or less can be used.

Secondary additives are usually added at 0.5-10 wt. %, and generally 0.1-3 wt. %. In one non-limiting embodiment, the amount of secondary additive is less than the primary additive; however, this is not required. For example, calcium can be added up to 10 wt. %, but is added normally at 0.5-3 wt. %. In most cases, the strengthening alloying additions or modifying materials are added in concentrations which can be greater than the high electronegativity corrosive phase forming element. The secondary additions are generally designed to have high solubility, and are added below their solid solubility limit in magnesium at the melting point, but above their solid solubility limit at some lower temperature. These form precipitates that strengthen the magnesium, and may or may not be galvanically active. They may form a precipitate by reacting preferentially with the high electronegativity addition (e.g., binary, ternary, or even quaternary intermetallics), with magnesium, or with other alloying additions.

The one or more secondary additives that have an electronegativity that is 1.25 or less have been found to form galvanically-active phases in the solid magnesium composite to enhance the dissolution rate of the magnesium composite in salt water, fracking liquid or brine environments. The inclusion of the one or more second additives with the one or more first additives in the molten magnesium or magnesium alloy has been found to enhance the dissolution rate of the magnesium composite by 1) alloying with inhibiting aluminum, zinc, magnesium, alloying additions and increasing the EMF driving force with the galvanically-active phase, and/or 2) reducing the electronegativity of the magnesium (e.g., α -magnesium) phase when placed in solid solution or magnesium-EPE (electropositive element) intermetallics. The addition of materials with an electronegativity that is less than magnesium, such as rare earths, group I, and group II, and group III elements on the periodic table, can enhance the degradability of the alloy when a high

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electronegativity addition is also present by reducing the electronegativity (increasing the driving force) in solid solution in magnesium, and/or by forming lower electronegativity precipitates that interact with the higher electronegativity precipitates. This technique/additions is particularly effective at reducing the sensitivity of the corrosion rates to temperature or salt content of the corroding or downhole fluid.

The addition of both electropositive (1.5 or greater) first additives and electronegative (1.25 or less) second additives to the molten magnesium or magnesium alloy can result in higher melting phases being formed in the magnesium composite. These higher melting phases can create high melt viscosities and can dramatically increase the temperature (and therefore the energy input) required to form the low viscosity melts suitable for casting. By dramatically increasing the casting temperature to above 700-780° C., or utilizing pressure to drive mold filling (e.g., squeeze casting), such processes can be used to produce a high quality, low-inclusion and low-porosity magnesium composite casting.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The artificial aging process (when used) can be for at least about 1 hour, for about 1-50 hours (and all values and ranges therebetween), for about 1-20 hours, or for about 8-20 hours. The solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours (and all values and ranges therebetween), for about 1-20 hours, or for about 8-20 hours. When an alloy with a galvanically-active phase (higher and/or lower electronegativity than Mg) with significant solid solubility is solutionized, substantial differences in corrosion/degradation rates can be achieved through mechanisms of oswald ripening or grain growth (coarsening of the active phases), which increases corrosion rates by 10-100% (and all values and ranges therebetween). When the solutionizing removes active phase and places it in solid solution, or creates finer precipitates (refined grain sizes), corrosion rates are decreased by 10-50%, up to about 75%.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content is at least about 75% and at least about 0.05 wt. % nickel is added to form in situ precipitation in the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. (and all values and ranges therebetween) for a period of 0.25-50 hours (and all values and ranges therebetween), the magnesium composite being characterized by higher dissolution rates than metal without nickel additions subjected to the said artificial aging process.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the magnesium content is at least about 85% and at least about 0.05 wt. % nickel is added to form in situ precipitation in the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature at about 100-500° C. (and all values and ranges therebetween) for a period of 0.25-50 hours, the magnesium composite being characterized by

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higher tensile and yield strengths than magnesium base alloys of the same composition, not including the amount of nickel.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content in the alloy is at least about 75% and at least about 0.05 wt. % copper is added to form in situ precipitation in the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said artificial aging process.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes the addition of calcium to galvanically-active magnesium-aluminum-(X) alloys with X being a galvanically-active intermetallic forming phase such as, but not limited to, nickel, copper, or cobalt to further control the degradation rate of the alloys, further increase the use and extrusion temperature of the magnesium composite, and/or reduce the potential for flammability during formation of the magnesium composite, thereby increasing safety. Calcium has a higher standard electrode potential than magnesium at -2.87V as compared to -2.37V for magnesium relative to standard hydrogen electrode (SHE). This electrode potential of calcium makes the galvanic potential between other metallic ions significantly higher, such as nickel (-0.25V), copper (+0.52V) and iron (-0.44V). The difference in galvanic potential also depends on other alloying elements with respect to microstructural location. In alloys where only magnesium and calcium are present, the difference in galvanic potential can change the degradation behavior of the alloy by leading to a greater rate of degradation in the alloy. However, the mechanism for dissolution speed change in the galvanically-active alloys created by intermetallic phases such as magnesium-nickel, magnesium-copper, and magnesium-cobalt is actually different. In the case of the magnesium-aluminum-calcium-(X) with X being a galvanically-active intermetallic forming phase such as nickel, copper, or cobalt with aluminum in the alloy, the calcium typically bonds with the aluminum (-1.66V), and this phase precipitates next to the magnesium matrix. The $Mg_{17}Al_{12}$ phase that is normally precipitated in a magnesium-aluminum-(X) with X being a galvanically-active intermetallic forming phase such as nickel, copper, or cobalt alloy is the primary contributor to a reduced and controlled degradation of the alloy.

By introducing calcium into the alloy, the amount of $Mg_{17}Al_{12}$ is reduced in the alloy, thus increasing the ratio of magnesium-(X) phase to the pure magnesium alloy and thereby reducing the galvanic corrosion resistance of the $Mg_{17}Al_{12}$ phase, which result in the further increase of the degradation rate of the magnesium-aluminum-calcium-(X) alloy as compared to magnesium-aluminum-(X) alloys. This feature of the alloy is new and unexpected because it is not just the addition of a higher standard electrode potential that is causing the degradation, but is also the reduction of a corrosion inhibitor by causing the formation of a different phase in the alloy. The calcium addition within the magnesium alloy forms an alternative phase with aluminum alloying elements. The calcium bonds with aluminum within the alloy to form lamellar Al_2Ca precipitates along the grain boundary of the magnesium matrix. These precipitates act as nucleation sites during cooling (due to their low energy barrier for nucleation) leading to decreased grain size and

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thereby higher strength for the magnesium alloy. However, the lamellar precipitates on a microscopic level tend to shear or cut into the alloy matrix and lead to crack propagation and can offset the beneficial strengthening of the grain refinement if an excessive amount of the AbCa phase is formed. The offsetting grain structure effects typically lead to a minimal improvement on tensile strength of the magnesium-aluminum-calcium alloy, if any. This seems to lead to no significant reduction in tensile strength of the alloy. The significant advantage for the addition of calcium in a magnesium-aluminum alloy is in the improved incipient melting temperature when the Al_2Ca phase is formed as opposed to $Mg_{17}Al_{12}$. Al_2Ca has a melting temperature of approximately 1080° C. as opposed to 460° C. for the magnesium-aluminum phase, which means a higher incipient melting point for the alloy. This solution leads to a larger hot deformation processing window or, more specifically, greater speeds during extrusion or rolling. These greater speeds can lead to lower cost production and a safer overall product. Another benefit of the calcium addition into the alloy is reduced oxidation of the melt. This feature is a result of the CaO layer which forms on the surface of the melt. In melt protection, the thickness and density of the calcium layer benefits the melt through formation of a reinforced CaO — MgO oxide layer when no other elements are present. This layer reduces the potential for “burning” in the foundry, thus allows for higher casting temperatures, reduced cover gas, reduced flux use and improved safety and throughput. The oxide layer also significantly increases the ignition temperature by eliminating the magnesium oxide layer typically found on the surface and replacing it with the much more stable CaO . The calcium addition in the magnesium alloy is generally at least 0.05 wt. % and generally up to about 30 wt. % (and all values and ranges therebetween), and typically 0.1-15 wt. %.

The developed alloys can be degraded in solutions with salt contents as low as 0.01% at a rate of 1-100 mg/cm²-hr. (and all values and ranges therebetween) at a temperature of 20-100° C. (and all values and ranges therebetween). The calcium additions work to enhance degradation in this alloy system, not by traditional means of adding a higher standard electrode potential material as would be common practice, but by actually reducing the corrosion inhibiting phase of $Mg_{17}Al_{12}$ by the precipitation of Al_2Ca phases that are mechanically just as strong, but do not inhibit the corrosion. As such, alloys can be created with higher corrosion rates just as alloys can be created by reducing aluminum content, but without strength degradation and the added benefit of higher use temperature, higher incipient melting temperatures and/or lower flammability. The alloy is a candidate for use in all degradation applications such as downhole tools, temporary structures, etc. where strength and high use temperature are a necessity and it is desirable to have a greater rate of dissolving or degradation rates in low-salt concentration solutions.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the total content of magnesium in the magnesium or magnesium alloy is at least about 85 wt. % and copper is added to form in situ precipitation in the magnesium or magnesium composite and solutionizing the resultant metal at a temperature of about 100-500° C. for a period of 0.25-50 hours. The magnesium composite is characterized by higher tensile and yield strengths than magnesium-based alloys of the same composition, but not including the amount of copper.

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In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable ball or frac ball in hydraulic fracturing and well drilling.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable tool for use in well drilling and hydraulic control as well as hydraulic fracturing.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that has controlled dissolution or degradation for use in temporarily isolating a wellbore.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that can be used to partially or full form a mandrel, slip, grip, ball, frac ball, dart, sleeve, carrier, or other downhole well component.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that can be used for controlling fluid flow or mechanical activation of a downhole device.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes secondary in situ formed reinforcements that are not galvanically active to the magnesium or magnesium alloy matrix to increase the mechanical properties of the magnesium composite. The secondary in situ formed reinforcements can optionally include a Mg_2Si phase as the in situ formed reinforcement.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a greater rate of cooling from the liquidus to the solidus point to create smaller in situ formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a slower rate of cooling from the liquidus to the solidus point to create larger in situ formed particles.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The artificial aging process (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours. The solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content is at least about 75 wt. % and at least 0.05 wt. % nickel is added to form in situ precipitation in the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without nickel additions subjected to the said artificial aging process.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the magnesium content is at least about 85 wt. % and at least 0.05 wt. % nickel is added to form in situ precipitation in the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature at about 100-500° C. for a period of 0.25-50 hours, the magnesium composite being charac-

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terized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of nickel.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content in the alloy is at least about 75 wt. % and at least 0.05 wt. % copper is added to form in situ precipitation in the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said artificial aging process.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the total content of magnesium in the magnesium or magnesium alloy is at least about 85 wt. % and at least 0.05 wt. % copper is added to form in situ precipitation in the magnesium or magnesium composite and solutionizing the resultant metal at a temperature of about 100-500° C. for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of copper.

In still another and/or alternative non-limiting aspect of the invention, the additive generally has a solubility in the molten magnesium or magnesium alloy of less than about 10% (e.g., 0.01-9.99% and all values and ranges therebetween), typically less than about 5%, more typically less than about 1%, and even more typically less than about 0.5%.

In still another and/or alternative non-limiting aspect of the invention, the additive can optionally have a surface area of 0.001-200 m²/g (and all values and ranges therebetween). The additive in the magnesium composite can optionally be less than about 1 µm in size (e.g., 0.001-0.999 µm and all values and ranges therebetween), typically less than about 0.5 µm, more typically less than about 0.1 µm, and more typically less than about 0.05 µm. The additive can optionally be dispersed throughout the molten magnesium or magnesium alloy using ultrasonic means, electrowetting of the insoluble particles, and/or mechanical agitation. In one non-limiting embodiment, the molten magnesium or magnesium alloy is subjected to ultrasonic vibration and/or waves to facilitate in the dispersion of the additive in the molten magnesium or magnesium alloy.

In still yet another and/or alternative non-limiting aspect of the invention, a plurality of additives in the magnesium composite are located in grain boundary layers of the magnesium composite.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a magnesium composite that includes a) providing magnesium or a magnesium alloy, b) providing one or more additives that have a low solubility when added to magnesium or a magnesium alloy when in a molten state; c) mixing the magnesium or a magnesium alloy and the one or more additives to form a mixture and to cause the one or more additives to disperse in the mixture; and d) cooling the mixture to form the magnesium composite. The step of mixing optionally includes mixing using one or more processes selected from the group consisting of thixomolding, stir casting, mechanical agitation, electrowetting and ultrasonic dispersion. The method optionally includes the step of heat treating the magnesium composite to improve the

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tensile strength, elongation, or combinations thereof of the magnesium composite without significantly affecting a dissolution rate of the magnesium composite. The method optionally includes the step of extruding or deforming the magnesium composite to improve the tensile strength, elongation, or combinations thereof of the magnesium composite without significantly affecting a dissolution rate of the magnesium composite. The method optionally includes the step of forming the magnesium composite into a device that a) facilitates in separating hydraulic fracturing systems and zones for oil and gas drilling, b) provides structural support or component isolation in oil and gas drilling and completion systems, or c) is in the form of a frac ball, valve, or degradable component of a well composition tool or other tool. Other types of structures that the magnesium composite can be partially or fully formed into include, but are not limited to, sleeves, valves, hydraulic actuating tooling and the like. Such non-limiting structures or additional non-limiting structure are illustrated in U.S. Pat. Nos. 8,905,147; 8,717,268; 8,663,401; 8,631,876; 8,573,295; 8,528,633; 8,485,265; 8,403,037; 8,413,727; 8,211,331; 7,647,964; US Publication Nos. 2013/0199800; 2013/0032357; 2013/0029886; 2007/0181224; and WO 2013/122712, all of which are incorporated herein by reference.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable ball or frac ball in hydraulic fracturing and well drilling.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable tool for use in well drilling and hydraulic control as well as hydraulic fracturing.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes secondary in situ formed reinforcements that are not galvanically active to the magnesium or magnesium alloy matrix to increase the mechanical properties of the magnesium composite. The secondary in situ formed reinforcements include a Mg₂Si phase or silicon particle phase as the in situ formed reinforcement.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a greater rate of cooling from the liquidus to the solidus point to create smaller in situ formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a slower cooling rate from the liquidus to the solidus point to create larger in situ formed particles.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The artificial aging process (when used) can be for at least about 1 hour, for about 1-50 hours (and all values and ranges therebetween), for about 1-20 hours, or for about 8-20 hours. Solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours (and all values and ranges therebetween), for about 1-20 hours, or for about 8-20 hours.

In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to mechanical agitation during the cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

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In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to chemical agitation during the cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to ultrasonic agitation during the cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to deformation or extrusion to further improve dispersion of the in situ formed particles.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that has a dissolve rate or dissolution rate of at least about 30 mg/cm²-hr in 3% KCl solution at 90° C., and typically 30-500 mg/cm²-hr in 3% KCl solution at 90° C. (and all values and ranges therebetween).

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that has a dissolve rate or dissolution rate of at least about 0.2 mg/cm²-min in a 3% KCl solution at 90° C., and typically 0.2-150 mg/cm²-min in a 3% KCl solution in at 90° C. (and all values and ranges therebetween).

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that has a dissolve rate or dissolution rate of at least about 0.1 mg/cm²-hr in a 3% KCl solution at 21° C., and typically 0.1-5 mg/cm²-hr in a 3% KCl solution at 21° C. (and all values and ranges therebetween).

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that has a dissolve rate or dissolution rate of at least about 0.2 mg/cm²-min in a 3% KCl solution at 20° C.

In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that has a dissolve rate or dissolution rate of at least about 0.1 mg/cm²-hr in 3% KCl solution at 20° C., typically 0.1-5 mg/cm²-hr in a 3% KCl solution at 20° C. (and all values and ranges therebetween).

In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800° C., c) adding up to about 7 wt. % nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 14 ksi, and an elongation of about 3% and a shear strength of 11 ksi. The cast material has a dissolve rate of about 75 mg/cm²-min in a 3% KCl solution at 90° C. The cast material dissolves at a rate of 1 mg/cm²-hr in a 3% KCl solution at 21° C. The cast material dissolves at a rate of 325 mg/cm²-hr. in a 3% KCl solution at 90° C. The cast material can be subjected to extrusion with an 11:1 reduction area. The extruded cast material exhibits a tensile strength of 40 ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm²-min in a 3% KCl solution at 20° C. The extruded cast material dissolves at a rate of 100

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mg/cm²-hr. in a 3% KCl solution at 90° C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100-200° C. The aged and extruded cast material exhibits a tensile strength of 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi. The aged extruded cast material dissolves at a rate of 110 mg/cm²-hr in 3% KCl solution at 90° C. and 1 mg/cm²-hr in 3% KCl solution at 20° C. The cast material can be subjected to a solutionizing treatment T4 for about 18 hours between 400-500° C. and then subjected to an artificial T6 age treatment for about 16 hours between 100-200° C. The aged and solutionized cast material exhibits a tensile strength of about 34 ksi, an elongation to failure of about 11%, and a shear strength of about 18 ksi. The aged and solutionized cast material dissolves at a rate of about 84 mg/cm²-hr in 3% KCl solution at 90° C., and about 0.8 mg/cm²-hr in 3% KCl solution at 20° C.

In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800° C., c) adding up to about 1 wt. % nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 18 ksi, and an elongation of about 5% and a shear strength of 17 ksi. The cast material has a dissolve rate of about 45 mg/cm²-min in a 3% KCl solution at 90° C. The cast material dissolves at a rate of 0.5 mg/cm²-hr. in a 3% KCl solution at 21° C. The cast material dissolves at a rate of 325 mg/cm²-hr. in a 3% KCl solution at 90° C. The cast material is subjected to extrusion with a 20:1 reduction area. The extruded cast material exhibits a tensile yield strength of 35 ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm²-min in a 3% KCl solution at 20° C. The extruded cast material dissolves at a rate of 50 mg/cm²-hr in a 3% KCl solution at 90° C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100-200° C. The aged and extruded cast material exhibits a tensile strength of 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having about 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800° C., c) adding about 10 wt. % copper to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of copper, d) dispersing the copper in the melted AZ91D magnesium alloy using chemical mixing agents at a temperature that is less than the melting point of copper, and e) cooling casting the melted mixture in a steel mold. The cast material exhibits a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolves at a rate of about 50 mg/cm²-hr. in a 3% KCl solution at 90° C. The cast material dissolves at a rate of 0.6 mg/cm²-hr. in a 3% KCl solution at 21° C. The cast material can be subjected to an artificial T5 age treatment for about 16 hours at a temperature of 100-200° C. The aged cast material exhibits a tensile strength of 50 ksi, an

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elongation to failure of 5%, and a shear strength of 25 ksi. The aged cast material dissolved at a rate of 40 mg/cm²-hr in 3% KCl solution at 90° C. and 0.5 mg/cm²-hr in 3% KCl solution at 20° C.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) providing magnesium having a purity of at least 99.9%, b) providing antimony having a purity of at least 99.8%, c) adding the magnesium and antimony in the crucible (e.g., carbon steel crucible), d) optionally adding a flux to the top of the metals in the crucible, e) optionally heating the metals in the crucible to 250° C. for about 2-60 minutes, f) heating the metals in the crucible to 650-720° C. to cause the magnesium to melt, and g) cooling the molten magnesium to form a magnesium composite that includes about 7 wt. % antimony. The density of the magnesium composite is 1.69 g/cm³, the hardness is 6.8 Rockwell Hardness B, and the dissolution rate in 3% solution of KCl at 90° C. is 20.09 mg/cm²-hr.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) providing magnesium having a purity of at least 99.9%, b) providing gallium having a purity of at least 99.9%, c) adding the magnesium and gallium in the crucible (e.g., carbon steel crucible), d) optionally adding a flux to the top of the metals in the crucible, e) optionally heating the metals in the crucible to 250° C. for about 2-60 minutes, f) heating the metals in the crucible to 650-720° C. to cause the magnesium to melt, and g) cooling the molten magnesium to form a magnesium composite that includes about 5 wt. % gallium. The density of the magnesium composite is 1.80 g/cm³, the hardness is 67.8 Rockwell Hardness B, and the dissolution rate in 3% solution of KCl at 90° C. is 0.93 mg/cm²-hr.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) providing magnesium having a purity of at least 99.9%, b) providing tin having a purity of at least 99.9%, c) adding the magnesium and tin in the crucible (e.g., carbon steel crucible), d) optionally adding a flux to the top of the metals in the crucible, e) optionally heating the metals in the crucible to 250° C. for about 2-60 minutes, f) heating the metals in the crucible to 650-720° C. to cause the magnesium to melt, and g) cooling the molten magnesium to form a magnesium composite that includes about 13 wt. % tin. The density of the magnesium composite is 1.94 g/cm³, the hardness is 75.6 Rockwell Hardness B, and the dissolution rate in 3% solution of KCl at 90° C. is 0.02 mg/cm²-hr.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) providing magnesium having a purity of at least 99.9%, b) providing bismuth having a purity of at least 99.9%, c) adding the magnesium and bismuth in the crucible (e.g., carbon steel crucible), d) optionally adding a flux to the top of the metals in the crucible, e) optionally heating the metals in the crucible to 250° C. for about 2-60 minutes, f) heating the metals in the crucible to 650-720° C. to cause the magnesium to melt, and g) cooling the molten magnesium to form a magnesium composite that includes about 10 wt. % bismuth. The density of the magnesium composite is 1.86 g/cm³, the hardness is 16.9 Rockwell Hardness B, and the dissolution rate in 3% solution of KCl at 90° C. is 26.51 mg/cm²-hr.

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In still another and/or alternative non-limiting aspect of the invention, there is provided dissolvable magnesium alloy in which additions of high electronegative intermetallic formers are selected from one or more elements with an electronegativity of greater than 1.75 and 0.2-5 wt. % of one or more elements with an electronegativity of 1.25 or less, a magnesium content in said magnesium alloy is greater than 50 wt. %, said one or more elements with an electronegativity of greater than 1.75 form a precipitate, particle, and/or intermetallic phase in said magnesium alloy, said one or more elements with an electronegativity of greater than 1.75 include one or more elements selected from the group of tin, nickel, iron, cobalt, silicon, nickel, chromium, copper, bismuth, lead, tin, antimony, indium, silver, aluminum, gold, platinum, cadmium, selenium, arsenic, boron, germanium, carbon, molybdenum, tungsten, manganese, zinc, rhenium, and gallium, said one or more elements with an electronegativity of 1.25 or less selected from the group of calcium, strontium, barium, potassium, neodymium, cerium, sodium, lithium, cesium, yttrium, lanthanum, samarium, europium, gadolinium, terbium, dysprosium, holmium, and ytterbium.

In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution properties of a magnesium or a magnesium alloy comprising of the steps of: a) heating the magnesium or a magnesium alloy to a point above its solidus temperature; b) adding an additive to said magnesium or magnesium alloy while said magnesium or magnesium alloy is above said solidus temperature of magnesium or magnesium alloy to form a mixture, said additive including one or more first additives having an electronegativity of greater than 1.5, said additive constituting about 0.05-45 wt. % of said mixture; c) dispersing said additive in said mixture while said magnesium or magnesium alloy is above said solidus temperature of magnesium or magnesium alloy; and, d) cooling said mixture to form a magnesium composite, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases. The first additive can optionally have an electronegativity of greater than 1.8. The step of controlling a size of said in situ precipitated intermetallic phase can optionally be by controlled selection of a mixing technique during said dispersion step, controlling a cooling rate of said mixture, or combinations thereof. The magnesium or magnesium alloy can optionally be heated to a temperature that is less than said melting point temperature of at least one of said additives. The magnesium or magnesium alloy can be heated to a temperature that is greater than said melting point temperature of at least one of said additives. The additive can optionally include one or more metals selected from the group consisting of calcium, copper, nickel, cobalt, bismuth, silver, gold, lead, tin, antimony, indium, arsenic, mercury, and gallium. The additive can optionally include one or more metals selected from the group consisting of calcium, copper, nickel, cobalt, bismuth, tin, antimony, indium, and gallium. The additive can optionally include one or more second additives that have an electronegativity of less than 1.25. The second additive can optionally include one or more metals selected from the group consisting of strontium, barium, potassium, sodium, lithium, cesium, and the rare earth metals such as yttrium, lanthanum, samarium, europium, gadolinium, terbium, dysprosium, holmium, and ytterbium. The additive can optionally be formed of a single composition, and has an average particle diameter size of about 0.1-500 microns. At least a portion of said additive can optionally remain at least partially in solution in an α -magnesium phase of said magnesium composite. The magnesium alloy can optionally

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include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, manganese in an amount of about 0.15-2 wt. %; boron in amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %; boron in amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %. The step of solutionizing said magnesium composite can optionally occur at a temperature above 300° C. and below a melting temperature of said magnesium composite to improve tensile strength, ductility, or combinations thereof of said magnesium composite. The step of forming said magnesium composite into a final shape or near net shape can optionally be by a) sand casting, permanent mold casting, investment casting, shell molding, or other pressureless casting technique at a temperature above 730° C., 2) using either pressure addition or elevated pouring temperatures above 710° C., or 3) subjecting the magnesium composite to pressures of 2000-20,000 psi through the use of squeeze casting, thixomolding, or high pressure die casting techniques. The step of aging said magnesium composite can optionally be at a temperature of above 100° C. and below 300° C. to improve tensile strength of said magnesium composite. The magnesium composite can optionally have a hardness above 14 Rockwell Harness B. The magnesium composite can optionally have a dissolution rate of at least 5 mg/cm²-hr. in 3% KCl at 90° C. The additive metal can optionally include about 0.05-35 wt. % nickel. The additive can optionally include about 0.05-35 wt. % copper. The additive can optionally include about 0.05-35 wt. % antimony. The additive can optionally include about 0.05-35 wt. % gallium. The additive can optionally include about 0.05-35 wt. % tin. The additive can optionally include about 0.05-35 wt. % bismuth. The additive can optionally include about 0.05-35 wt. % calcium. The method can optionally further include the step of rapidly solidifying said magnesium composite by atomizing the molten mixture and then subjecting the atomized molten mixture to ribbon casting, gas and water atomization, pouring into a liquid, high speed machining, saw cutting, or grinding into chips, followed by powder or chip consolidation below its liquidus temperature.

In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases comprising a magnesium or a magnesium alloy and an additive constituting about 0.05-45 wt. % of said magnesium composite, said magnesium having a content in said magnesium composite that is greater than 50 wt. %, said additive forming metal composite particles or precipitant in said magnesium composite, said metal composite particles or precipitant forming said in situ precipitation of said galvanically-active intermetallic phases, said additive including one or more first additives having an electronegativity of 1.5 or greater. The magnesium composite can optionally further include one or more second additives having an electronegativity of 1.25 or less. The first additive can optionally have an electronegativity of greater than 1.8.

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The first additive can optionally include one or more metals selected from the group consisting of copper, nickel, cobalt, bismuth, silver, gold, lead, tin, antimony, indium, arsenic, mercury, and gallium. The first additive can optionally include one or more metals selected from the group consisting of copper, nickel, cobalt, bismuth, tin, antimony, indium, and gallium. The second additive can optionally include one or more metals selected from the group consisting of calcium, strontium, barium, potassium, sodium, lithium, cesium, and the rare earth metals such as yttrium, lanthanum, samarium, europium, gadolinium, terbium, dysprosium, holmium, and ytterbium. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %. The additive can optionally include about 0.05-45 wt. % nickel. The first additive can optionally include about 0.05-45 wt. % copper. The first additive can optionally include about 0.05-45 wt. % cobalt. The first additive can optionally include about 0.05-45 wt. % antimony. The first additive can optionally include about 0.05-45 wt. % gallium. The first additive can optionally include about 0.05-45 wt. % tin. The first additive can optionally include about 0.05-45 wt. % bismuth. The second additive can optionally include 0.05-35 wt. % calcium. The magnesium composite can optionally have a hardness above 14 Rockwell Harness B. The magnesium composite can optionally have a dissolution rate of at least 5 mg/cm²-hr. in 3% KCl at 90° C. The magnesium composite can optionally have a dissolution rate of about 5-300 mg/cm²-hr in 3 wt. % KCl water mixture at 90° C. The magnesium composite can optionally be subjected to a surface treatment to improve a surface hardness of said magnesium composite, said surface treatment including peening, heat treatment, aluminizing, or combinations thereof. A dissolution rate of said magnesium composite can optionally be controlled by an amount and size of said in situ formed galvanically-active particles whereby smaller average sized particles of said in situ formed galvanically-active particles, a greater weight percent of said in situ formed galvanically-active particles in said magnesium composite, or combinations thereof increases said dissolution rate of said magnesium composite.

In still another and/or alternative non-limiting aspect of the invention, there is provided a dissolvable component for use in downhole operations that is fully or partially formed of a magnesium composite, said dissolvable component including a component selected from the group consisting of sleeve, frac ball, hydraulic actuating tooling, mandrel, slip, grip, ball, dart, carrier, tube, valve, valve component, plug, or other downhole well component, said magnesium composite includes in situ precipitation of galvanically-active intermetallic phases comprising a magnesium or a magnesium alloy and an additive constituting about 0.05-45 wt. % of said magnesium composite, said magnesium having a content in said magnesium composite that is greater than 50 wt. %, said additive forming metal composite particles or precipitant in said magnesium composite, said metal composite particles or precipitant forming said in situ precipitation of said galvanically-active intermetallic phases, said additive including one or more first additives having an electronegativity of 1.5 or greater. The dissolvable compo-

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nent can optionally further include one or more second additives having an electronegativity of 1.25 or less. The first additive can optionally have an electronegativity of greater than 1.8. The first additive can optionally include one or more metals selected from the group consisting of copper, nickel, cobalt, bismuth, silver, gold, lead, tin, antimony, indium, arsenic, mercury, and gallium. The first additive can optionally include one or more metals selected from the group consisting of copper, nickel, cobalt, bismuth, tin, antimony, indium, and gallium. The second additive can optionally include one or more metals selected from the group consisting of calcium, strontium, barium, potassium, sodium, lithium, cesium, and the rare earth metals such as yttrium, lanthanum, samarium, europium, gadolinium, terbium, dysprosium, holmium, and ytterbium. The second additive can optionally include 0.05-35 wt. % calcium. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese. The magnesium composite can optionally have a hardness above 14 Rockwell Harness B. The magnesium composite can optionally have a dissolution rate of at least 5 mg/cm²-hr. in 3% KCl at 90° C. The magnesium composite can optionally have a dissolution rate of at least 10 mg/cm²-hr in a 3% KCl solution at 90° C. The magnesium composite can optionally have a dissolution rate of at least 20 mg/cm²-hr in a 3% KCl solution at 65° C. The magnesium composite can optionally have a dissolution rate of at least 1 mg/cm²-hr in a 3% KCl solution at 65° C. The magnesium composite can optionally have a dissolution rate of at least 100 mg/cm²-hr in a 3% KCl solution at 90° C. The magnesium composite can optionally have a dissolution rate of at least 45 mg/cm²-hr. in 3 wt. % KCl water mixture at 90° C. and up to 325 mg/cm²-hr. in 3 wt. % KCl water mixture at 90° C. The magnesium composite can optionally have a dissolution rate of up to 1 mg/cm²-hr. in 3 wt. % KCl water mixture at 21° C. The magnesium composite can optionally have a dissolution rate of at least 90 mg/cm²-hr. in 3% KCl solution at 90° C. The magnesium composite can optionally have a dissolution rate of at least a rate of 0.1 mg/cm²-hr. in 0.1% KCl solution at 90° C. The magnesium composite can optionally have a dissolution rate of a rate of <0.1 mg/cm²-hr. in 0.1% KCl solution at 75° C. The magnesium composite can optionally have a dissolution rate of, a rate of <0.1 mg/cm²-hr. in 0.1% KCl solution at 60° C. The magnesium composite can optionally have a dissolution rate of <0.1 mg/cm²-hr. in 0.1% KCl solution at 45° C. The magnesium composite can optionally have a dissolution rate of at least 30 mg/cm²-hr. in 0.1% KCl solution at 90° C. The magnesium composite can optionally have a dissolution rate of at least 20 mg/cm²-hr. in 0.1% KCl solution at 75° C. The magnesium composite can optionally have a dissolution rate of at least 10 mg/cm²-hr. in 0.1% KCl solution at 60° C. The magnesium composite can optionally have a dissolution rate of at least 2 mg/cm²-hr. in 0.1% KCl solution at 45° C. The metal composite particles or precipitant in said magnesium composite can optionally have a solubility in said magnesium of less than 5%. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in an amount of about 0.1-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in an amount of about 0.0002-0.04 wt. %, and

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bismuth in amount of about 0.4-0.7 wt. %. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt. %, zinc in an amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %, boron in an amount of about 0.0002-0.04 wt. %, and bismuth in an amount of about 0.4-0.7 wt. %. The magnesium alloy can optionally include at least 85 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese. The magnesium alloy can optionally include 60-95 wt. % magnesium and 0.01-1 wt. % zirconium. The magnesium alloy can optionally include 60-95 wt. % magnesium, 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, and 0.15-2 wt. % manganese. The magnesium alloy can optionally include 60-95 wt. % magnesium, 0.05-6 wt. % zinc, and 0.01-1 wt. % zirconium. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese. The magnesium alloy can optionally include over 50 wt. % magnesium and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable magnesium alloy including 1-15 wt. % aluminum and a dissolution enhancing intermetallic phase between magnesium and cobalt, nickel, and/or copper with the alloy composition containing 0.05-25 wt. % cobalt, nickel, and/or copper, and 0.1-15 wt. % calcium.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable magnesium alloy including 1-15 wt. % aluminum and a dissolution enhancing intermetallic phase between magnesium and cobalt, nickel, and/or copper with the alloy composition containing 0.05-25 wt. % cobalt, nickel, and/or copper, and 0.1-15 wt. % of calcium, strontium, barium and/or scandium.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable magnesium alloy wherein the alloy composition includes 0.5-8 wt. % calcium, 0.05-20 wt. % nickel, 3-11 wt. % aluminum, and 50-95 wt. % magnesium and the alloy degrades at a rate that is greater than 5 mg/cm²-hr. at temperatures below 90° C. in fresh water (water with less than 1000 ppm salt content).

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable magnesium alloy wherein the alloy composition includes 0-2 wt. % zinc, 0.5-8 wt. % calcium, 0.05-20 wt. % nickel, 5-11 wt. % aluminum, and 50-95 wt. % magnesium and the alloy degrades at a rate that is greater than 1 mg/cm²-hr. at temperatures below 45° C. in fresh water (water with less than 1000 ppm salt content).

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally include calcium, strontium and/or barium addition that forms an aluminum-calcium phase, an aluminum-strontium phase and/or an aluminum-barium phase that leads to an alloy with a higher incipient melting point and increased corrosion rate.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally include calcium that creates an aluminum-cal-

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cium (e.g., AlCa_2 phase) as opposed to a magnesium-aluminum phase (e.g., $\text{Mg}_{17}\text{Al}_{12}$ phase) to thereby enhance the speed of degradation of the alloy when exposed to a conductive fluid vs. the common practice of enhancing the speed of degradation of an aluminum-containing alloy by reducing the aluminum content to reduce the amount of $\text{Mg}_{17}\text{Al}_{12}$ in the alloy.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally include calcium addition that forms an aluminum-calcium phase that increases the ratio of dissolution of intermetallic phase to the base magnesium, and thus increases the dissolution rate of the alloy.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally include calcium addition that forms an aluminum-calcium phase reduces the salinity required for the same dissolution rate by over $2\times$ at 90°C . in a saline solution.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally include calcium addition that increases the incipient melting temperature of the degradable alloy, thus the alloy can be extruded at higher speeds and thinner walled tubes can be formed as compared to a degradable alloy without calcium additions.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy wherein the mechanical properties of tensile yield and ultimate strength are optionally not lowered by more than 10% or are enhanced as compared to an alloy without calcium addition.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy wherein the elevated mechanical properties of yield strength and ultimate strength of the alloy at temperatures above 100°C . are optionally increased by more than 5% due to the calcium addition.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy wherein the galvanically active phase is optionally present in the form of an LPSO (Long Period Stacking Fault) phase such as $\text{Mg}_{12}\text{Zn}_{1-x}\text{Ni}_x\text{RE}$ (where RE is a rare earth element) and that phase is 0.05-5 wt. % of the final alloy composition.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy wherein the mechanical properties at 150°C . are optionally at least 24 ksi tensile yield strength, and are not less than 20% lower than the mechanical properties at room temperature (77°F .).

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy wherein the dissolution rate at 150°C . in 3% KCl brine is optionally 10-150 $\text{mg}/\text{cm}^2/\text{hr}$.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy that optionally can include 2-4 wt. % yttrium, 2-5 wt. % gadolinium, 0.3-4 wt. % nickel, and 0.05-4 wt. % zinc.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy that can optionally include 0.1-0.8 wt. % manganese and/or zirconium.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy that can optionally be used in downhole applications such as pressure segmentation, or zonal control.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally be used for zonal or pressure isolation in a downhole component or tool.

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In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a degradable alloy wherein a base dissolution of enhanced magnesium alloy is optionally melted and calcium is added as metallic calcium above the liquids of the magnesium-aluminum phase and the aluminum preferentially forms AlCa_2 vs. $\text{Mg}_{17}\text{Al}_{12}$ during solidification of the alloy.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally be formed by adding calcium is in the form of an oxide or salt that is reduced by the molten melt vs. adding the calcium as a metallic element.

In still another and/or alternative non-limiting aspect of the invention, there is provided a degradable alloy can optionally be formed at double the speed or higher as compared to an alloy that does not include calcium due to the rise in incipient melting temperature.

One non-limiting objective of the present invention is the provision of a castable, moldable, or extrudable magnesium composite formed of magnesium or magnesium alloy and one or more additives dispersed in the magnesium or magnesium alloy.

Another and/or alternative non-limiting objective of the present invention is the provision of selecting the type and quantity of one or more additives so that the grain boundaries of the magnesium composite have a desired composition and/or morphology to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite.

Still yet another and/or alternative non-limiting objective of the present invention is the provision of forming a magnesium composite wherein the one or more additives can be used to enhance mechanical properties of the magnesium composite, such as ductility and/or tensile strength.

Another and/or alternative non-limiting objective of the present invention is the provision of forming a magnesium composite that can be enhanced by heat treatment as well as deformation processing, such as extrusion, forging, or rolling, to further improve the strength of the final magnesium composite.

Yet another and/or alternative non-limiting objective of the present invention is the provision of forming a magnesium composite that can be made into almost any shape.

Another and/or alternative non-limiting objective of the present invention is the provision of dispersing the one or more additives in the molten magnesium or magnesium alloy is at least partially by thixomolding, stir casting, mechanical agitation, electrowetting, ultrasonic dispersion and/or combinations of these processes.

Another and/or alternative non-limiting objective of the present invention is the provision of producing a magnesium composite with at least one insoluble phase that is at least partially formed by the additive or additive material, and wherein the one or more additives have a different galvanic potential from the magnesium or magnesium alloy.

Still yet another and/or alternative non-limiting objective of the present invention is the provision of producing a magnesium composite wherein the rate of corrosion in the magnesium composite can be controlled by the surface area via the particle size and morphology of the one or more additions.

Yet another and/or alternative non-limiting objective of the present invention is the provision of producing a magnesium composite that includes one or more additives that have a solubility in the molten magnesium or magnesium alloy of less than about 10%.

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Still yet another and/or alternative non-limiting objective of the present invention, there is provided a magnesium composite that can be used as a dissolvable, degradable and/or reactive structure in oil drilling.

These and other objects, features and advantages of the present invention will become apparent in light of the following detailed description of preferred embodiments thereof, as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1-3 show a typical cast microstructure with galvanically-active in situ formed intermetallic phase wetted to the magnesium matrix.

FIG. 4 shows a typical phase diagram to create in situ formed particles of an intermetallic $Mg_x(M)$, $Mg(M_x)$ and/or unalloyed M and/or M alloyed with another M where M is any element on the periodic table or any compound in a magnesium matrix and wherein M has a electronegativity that is 1.5 or greater and optionally includes one or more elements that have an electronegativity that is 1.25 or less.

FIG. 5 illustrates a MgSb7 alloy prior to and after being exposed to 3% solution KCl at 90° C. for 6 hr. The measured dissolution rate was 20.09 mg/cm²/hr. Prior to being exposed to the salt solution, the alloy had a density of 1.69 and a Rockwell B hardness of 16.9.

FIG. 6 illustrates a MgBi10 alloy prior to and after being exposed to 3% solution KCl at 90° C. for 6 hr. The measured dissolution rate was 26.51 mg/cm²/hr. Prior to being exposed to the salt solution, the alloy had a density of 1.86 and a Rockwell B hardness of 6.8.

DETAILED DESCRIPTION OF THE INVENTION

Referring now to the figures wherein the showings illustrate non-limiting embodiments of the present invention, the present invention is directed to a magnesium composite that includes one or more additives dispersed in the magnesium composite. The magnesium composite of the present invention can be used as a dissolvable, degradable and/or reactive structure in oil drilling. For example, the magnesium composite can be used to form a frac ball or other structure (e.g., sleeves, valves, hydraulic actuating tooling and the like, etc.) in a well drilling or completion operation. Although the magnesium composite has advantageous applications in the drilling or completion operation field of use, it will be appreciated that the magnesium composite can be used in any other field of use wherein it is desirable to form a structure that is controllably dissolvable, degradable and/or reactive.

The present invention is directed to a novel magnesium composite that can be used to form a castable, moldable, or extrudable component. The magnesium composite includes at least 50 wt. % magnesium. Generally, the magnesium composite includes over 50 wt. % magnesium and less than about 99.5 wt. % magnesium and all values and ranges therebetween. One or more additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention. The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives are added to the molten magnesium or magnesium alloy at a temperature that is typically less than

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the melting point of the one or more additives; however, this is not required. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are not caused to fully melt in the molten magnesium or magnesium alloy; however, this is not required. For additives that partially or fully melt in the molten magnesium or molten magnesium alloy, these additives form alloys with magnesium and/or other additives in the melt, thereby resulting in the precipitation of such formed alloys during the cooling of the molten magnesium or molten magnesium alloy to form the galvanically-active phases in the magnesium composite. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or magnesium alloy are cooled to form a solid magnesium component that includes particles in the magnesium composite. Such a formation of particles in the melt is called in situ particle formation as illustrated in FIGS. 1-3. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the in situ phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The in situ formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates through precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electrode potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the in situ formed particles size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of in situ particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. In situ particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques. A smaller particle size can be used to increase the dissolution rate of the magnesium composite. An increase in the weight percent of the in situ formed particles or phases in the magnesium composite can also or alternatively be used to increase the dissolution rate of the magnesium composite. A phase diagram for forming in situ formed particles or phases in the magnesium composite is illustrated in FIG. 4.

In accordance with the present invention, a novel magnesium composite is produced by casting a magnesium metal or magnesium alloy with at least one component to form a galvanically-active phase with another component in

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the chemistry that forms a discrete phase that is insoluble at the use temperature of the dissolvable component. The in situ formed particles and phases have a different galvanic potential from the remaining magnesium metal or magnesium alloy. The in situ formed particles or phases are uniformly dispersed through the matrix metal or metal alloy using techniques such as thixomolding, stir casting, mechanical agitation, chemical agitation, electrowetting, ultrasonic dispersion, and/or combinations of these methods. Due to the particles being formed in situ to the melt, such particles generally have excellent wetting to the matrix phase and can be found at grain boundaries or as continuous dendritic phases throughout the component depending on alloy composition and the phase diagram. Because the alloys form galvanic intermetallic particles where the intermetallic phase is insoluble to the matrix at use temperatures, once the material is below the solidus temperature, no further dispersing or size control is necessary in the component. This feature also allows for further grain refinement of the final alloy through traditional deformation processing to increase tensile strength, elongation to failure, and other properties in the alloy system that are not achievable without the use of insoluble particle additions. Because the ratio of in situ formed phases in the material is generally constant and the grain boundary to grain surface area is typically consistent even after deformation processing and heat treatment of the composite, the corrosion rate of such composites remains very similar after mechanical processing.

EXAMPLE 1

An AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc and 90 wt. % magnesium was melted to above 800° C. and at least 200° C. below the melting point of nickel. About 7 wt. % of nickel was added to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolved at a rate of about 75 mg/cm²-min in a 3% KCl solution at 90° C. The material dissolved at a rate of 1 mg/cm²-hr in a 3% KCl solution at 21° C. The material dissolved at a rate of 325 mg/cm²-hr. in a 3% KCl solution at 90° C.

EXAMPLE 2

The composite in Example 1 was subjected to extrusion with an 11:1 reduction area. The material exhibited a tensile yield strength of 45 ksi, an Ultimate tensile strength of 50 ksi and an elongation to failure of 8%. The material has a dissolve rate of 0.8 mg/cm²-min. in a 3% KCl solution at 20° C. The material dissolved at a rate of 100 mg/cm²-hr. in a 3% KCl solution at 90° C.

EXAMPLE 3

The alloy in Example 2 was subjected to an artificial T5 age treatment of 16 hours from 100-200° C. The alloy exhibited a tensile strength of 48 ksi and elongation to failure of 5% and a shear strength of 25 ksi. The material dissolved at a rate of 110 mg/cm²-hr. in 3% KCl solution at 90° C. and 1 mg/cm²-hr. in 3% KCl solution at 20° C.

EXAMPLE 4

The alloy in Example 1 was subjected to a solutionizing treatment T4 of 18 hours from 400° C.-500° C. and then an

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artificial T6 aging process of 16 hours from 100-200 C. The alloy exhibited a tensile strength of 34 ksi and elongation to failure of 11% and a shear strength of 18 Ksi. The material dissolved at a rate of 84 mg/cm²-hr. in 3% KCl solution at 90° C. and 0.8 mg/cm²-hr. in 3% KCl solution at 20° C.

EXAMPLE 5

An AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc, and 90 wt. % magnesium was melted to above 800° C. and at least 200° C. below the melting point of copper. About 10 wt. % of copper alloyed to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile yield strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolved at a rate of about 50 mg/cm²-hr. in a 3% KCl solution at 90° C. The material dissolved at a rate of 0.6 mg/cm²-hr. in a 3% KCl solution at 21° C.

EXAMPLE 6

The alloy in Example 5 was subjected to an artificial T5 aging process of 16 hours from 100-200° C. The alloy exhibited a tensile strength of 50 ksi and elongation to failure of 5% and a shear strength of 25 ksi. The material dissolved at a rate of 40 mg/cm²-hr. in 3% KCl solution at 90° C. and 0.5 mg/cm²-hr. in 3% KCl solution at 20° C.

EXAMPLE 7

An AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc, and 90 wt. % magnesium was melted to above 700° C. About 16 wt. % of 75 μm iron particles were added to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile strength of about 26 ksi, and an elongation of about 3%. The cast material dissolved at a rate of about 2.5 mg/cm²-min in a 3% KCl solution at 20° C. The material dissolved at a rate of 60 mg/cm²-hr in a 3% KCl solution at 65° C. The material dissolved at a rate of 325 mg/cm²-hr. in a 3% KCl solution at 90° C.

EXAMPLE 8

An AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc, and 90 wt. % magnesium was melted to above 700° C. About 2 wt. % 75 μm iron particles were added to the melt and dispersed. The melt was cast into steel molds. The material exhibited a tensile strength of 26 ksi, and an elongation of 4%. The material dissolved at a rate of 0.2 mg/cm²-min in a 3% KCl solution at 20° C. The material dissolved at a rate of 1 mg/cm²-hr in a 3% KCl solution at 65° C. The material dissolved at a rate of 10 mg/cm²-hr in a 3% KCl solution at 90° C.

EXAMPLE 9

An AZ91D magnesium alloy having 9 wt. % aluminum, 1 wt. % zinc, and 90 wt. % magnesium was melted to above 700° C. About 2 wt. % nano iron particles and about 2 wt. % nano graphite particles were added to the composite using ultrasonic mixing. The melt was cast into steel molds. The material dissolved at a rate of 2 mg/cm²-min in a 3% KCl solution at 20° C. The material dissolved at a rate of 20 mg/cm²-hr in a 3% KCl solution at 65° C. The material dissolved at a rate of 100 mg/cm²-hr in a 3% KCl solution at 90° C.

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EXAMPLE 10

The composite in Example 7 was subjected to extrusion with an 11:1 reduction area. The extruded metal cast structure exhibited a tensile strength of 38 ksi, and an elongation to failure of 12%. The extruded metal cast structure dissolved at a rate of 2 mg/cm²-min in a 3% KCl solution at 20° C. The extruded metal cast structure dissolved at a rate of 301 mg/cm²-min in a 3% KCl solution at 90° C. The extruded metal cast structure exhibited an improvement of 58% tensile strength and an improvement of 166% elongation with less than 10% change in dissolution rate as compared to the non-extruded metal cast structure.

EXAMPLE 11

Pure magnesium was melted to above 650° C. and below 750° C. About 7 wt. % of antimony was dispersed in the molten magnesium. The melt was cast into a steel mold. The cast material dissolved at a rate of about 20.09 mg/cm²-hr in a 3% KCl solution at 90° C.

EXAMPLE 12

Pure magnesium was melted to above 650° C. and below 750° C. About 5 wt. % of gallium was dispersed in the molten magnesium. The melt was cast into a steel mold. The cast material dissolved at a rate of about 0.93 mg/cm²-hr in a 3% KCl solution at 90° C.

EXAMPLE 13

Pure magnesium was melted to above 650° C. and below 750° C. About 13 wt. % of tin was dispersed in the molten magnesium. The melt was cast into a steel mold. The cast material dissolved at a rate of about 0.02 mg/cm²-hr in a 3% KCl solution at 90° C.

EXAMPLE 14

A magnesium alloy that included 9 wt. % aluminum, 0.7 wt. % zinc, 0.3 wt. % nickel, 0.2 wt. % manganese, and the balance magnesium was heated to 157° C. (315° F.) under an SF₆-CO₂ cover gas blend to provide a protective dry atmosphere for the magnesium alloy. The magnesium alloy was then heated to 730° C. to melt the magnesium alloy and calcium was then added into the molten magnesium alloy in an amount that the calcium constituted 2 wt. % of the mixture. The mixture of molten magnesium alloy and calcium was agitated to adequately disperse the calcium within the molten magnesium alloy. The mixture was then poured into a preheated and protective gas-filled steel mold and naturally cooled to form a cast part that was a 9"×32" billet. The billet was subsequently preheated to ~350° C. and extruded into a solid and tubular extrusion profile. The extrusions were run at 12 and 7 inches/minute respectively, which is 2×-3× faster than the maximum speed the same alloy achieved without calcium alloying. It was determined that once the molten mixture was cast into a steel mold, the molten surface of the mixture in the mold did not require an additional cover gas or flux protection during solidification. This can be compared to the same magnesium-aluminum alloy without calcium that requires either an additional cover gas or flux during solidification to prevent burning.

The effect of the calcium on the corrosion rate of a magnesium-aluminum-nickel alloy was determined. Since magnesium already has a high galvanic potential with

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nickel, the magnesium alloy corrodes rapidly in an electrolytic solution such as a potassium chloride brine. The KCl brine was a 3% solution heated to 90° C. (194° F.). The corrosion rate was compared by submerging 1"×0.6" samples of the magnesium alloy with and without calcium additions in the solution for 6 hours and the weight loss of the alloy was calculated relative to initial exposed surface area. The magnesium alloy that did not include calcium dissolved at a rate of 48 mg/cm²-hr. in the 3% KCl solution at 90° C. The magnesium alloy that included calcium dissolved at a rate of 91 mg/cm²-hr. in the 3% KCl solution at 90° C. The corrosion rates were also tested in fresh water. The fresh water is water that has up to or less than 1000 ppm salt content. A KCl brine solution was used to compare the corrosion rate of the magnesium alloy with and without calcium additions. 1"×0.6" samples of the magnesium alloy with and without calcium additions were submerged in the 0.1% KCl brine solution for 6 hours and the weight loss of the alloys were calculated relative to initial exposed surface area. The magnesium alloy that did not include calcium dissolved at a rate of 0.1 mg/cm²-hr. in the 0.1% KCl solution at 90° C., a rate of <0.1 mg/cm²-hr. in the 0.1% KCl solution at 75° C., a rate of <0.1 mg/cm²-hr. in the 0.1% KCl solution at 60° C., and a rate of <0.1 mg/cm²-hr. in the 0.1% KCl solution at 45° C. The magnesium alloy that did include calcium dissolved at a rate of 34 mg/cm²-hr. in the 0.1% KCl solution at 90° C., a rate of 26 mg/cm²-hr. in the 0.1% KCl solution at 75° C., a rate of 14 mg/cm²-hr. in the 0.1% KCl solution at 60° C., and a rate of 5 mg/cm²-hr. in the 0.1% KCl solution at 45° C.

The effect of calcium on magnesium alloy revealed that the microscopic "cutting" effect of the lamellar aluminum-calcium phase slightly decreases the tensile strength at room temperature, but increased tensile strength at elevated temperatures due to the grain refinement effect of Al₂Ca. The comparative tensile strength and elongation to failure are shown in Table A.

TABLE A

Test Temperature	Tensile Strength without Ca (psi)	Elongation to failure without Ca (%)	Tensile Strength with 2 wt. % Ca (psi)	Elongation to failure with 2 wt. % Ca (%)
25° C.	23.5	2.1	21.4	1.7
150° C.	14.8	7.8	16.2	6.8

The effect of varying calcium concentration in a magnesium-aluminum-nickel alloy was tested. The effect on ignition temperature and maximum extrusion speed was also tested. For mechanical properties, the effect of 0-2 wt. % calcium additions to the magnesium alloy on ultimate tensile strength (UTS) and elongation to failure (Ef) is illustrated in Table B.

TABLE B

Calcium Concentration (wt. %)	UTS at 25° C.	E _f at 25° C.	UTS at 150° C.	E _f at 150° C.
0%	41.6	10.3	35.5	24.5
0.5%	40.3	10.5	34.1	24.0
1.0%	38.5	10.9	32.6	23.3
2.0%	37.7	11.3	31.2	22.1

The effect of calcium additions in the magnesium-aluminum-nickel alloy on ignition temperature was tested and

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found to be similar to a logarithmic function, with the ignition temperature tapering off. The ignition temperature trend is shown in Table C.

TABLE C

	Calcium Concentration (wt. %)					
	0	1	2	3	4	5
Ignition Temperature (° C.)	550	700	820	860	875	875

The incipient melting temperature effect on maximum extrusion speeds was also found to trend similarly to the ignition temperature since the melting temperature of the magnesium matrix is limiting. The extrusion speed for a 4" solid round extrusion from at 9" round billet trends as shown in Table D.

TABLE D

Calcium Concentration (wt. %)	0%	0.5%	1%	2%	4%
Extrusion Speed for 4" solid (in/min)	4	6	9	12	14
Extrusion speed for 4.425" OD x 2.645" ID tubular (in/min)	1.5	2.5	4	7	9

EXAMPLE 15

Pure magnesium is heated to a temperature of 680-720° C. to form a melt under a protective atmosphere of SF₆+CO₂+air. 1.5-2 wt. % zinc and 1.5-2 wt. % nickel were added using zinc lump and pelletized nickel to form a molten solution. From 3-6 wt. % gadolinium, as well as about 3-6 wt. % yttrium was added as lumps of pure metal, and 0.5-0.8% zirconium was added as a Mg-25% zirconium master alloy to the molten magnesium, which is then stirred to distribute the added metals in the molten magnesium. The melt was then cooled to 680° C., and degassed using HCN and then poured in to a permanent A36 steel mold and solidified. After solidification of the mixture, the billet was solution treated at 500° C. for 4-8 hours and air cooled. The billet was reheated to 360° C. and aged for 12 hours, followed by extrusion at a 5:1 reduction ratio to form a rod.

It is known that LPSO phases in magnesium can add high temperature mechanical properties as well as significantly increase the tensile properties of magnesium alloys at all temperatures. The Mg₁₂Zn_{1-x}Ni_x RE₁ LPSO (long period stacking order) phase enables the magnesium alloy to be both high strength and high temperature capable, as well as to be able to be controllably dissolved using the phase as an in situ galvanic phase for use in activities where enhanced and controllable use of degradation is desired. Such activities include use in oil and gas wells as temporary pressure diverters, balls, and other tools that utilize dissolvable metals.

The magnesium alloy was solution treated at 500° C. for 12 hours and air-cooled to allow precipitation of the 14H LPSO phase incorporating both zinc and nickel as the transition metal in the layered structure. The solution-treated alloy was then preheated at 350-400° C. for over 12 hours prior to extrusion at which point the material was extruded using a 5:1 extrusion ratio (ER) with an extrusion speed of 20 ipm (inch per minute).

At the nano-layers present between the nickel and the magnesium layers or magnesium matrix, the galvanic reaction took place. The dissolution rate in 3% KCl brine

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solution at 90° C. as well as the tensile properties at 150° C. of the galvanically reactive alloy are shown in Table E.

TABLE E

Magnesium Alloy	Dissolution rate (mg/cm ² -hr.)	Ultimate Tensile Strength at 150° C. (ksi)	Tensile Yield Strength at 150° C. (ksi)	Elongation to Failure at 150° C. (%)
	62-80	36	24	38

Pure magnesium was melted to above 650° C. and below 750° C. About 10 wt. % of bismuth was dispersed in the molten magnesium. The melt was cast into a steel mold. The cast material dissolved at a rate of about 26.51 mg/cm²-hr in a 3% KCl solution at 90° C.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in the constructions set forth without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense. The invention has been described with reference to preferred and alternate embodiments. Modifications and alterations will become apparent to those skilled in the art upon reading and understanding the detailed discussion of the invention provided herein. This invention is intended to include all such modifications and alterations insofar as they come within the scope of the present invention. It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention, which, as a matter of language, might be said to fall there between. The invention has been described with reference to the preferred embodiments. These and other modifications of the preferred embodiments as well as other embodiments of the invention will be obvious from the disclosure herein, whereby the foregoing descriptive matter is to be interpreted merely as illustrative of the invention and not as a limitation. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims.

What is claimed:

1. A dissolvable magnesium alloy in which additions of high electronegative intermetallic formers are selected from one or more elements with an electronegativity of greater than 1.75 and 0.2-5 wt. % of one or more elements with an electronegativity of 1.25 or less, a magnesium content in said dissolvable magnesium alloy is greater than 50 wt. %, said one or more elements with an electronegativity of greater than 1.75 form a precipitate, particle, and/or intermetallic phase in said dissolvable magnesium alloy, said one or more elements with an electronegativity of greater than 1.75 include one or more elements selected from the group of tin, nickel, iron, cobalt, silicon, nickel, chromium, copper, bismuth, lead, tin, antimony, indium, silver, aluminum, gold, platinum, cadmium, selenium, arsenic, boron, germanium, carbon, molybdenum, tungsten, manganese, zinc, rhenium and gallium, said one or more elements with an electronegativity of 1.25 or less are selected from the group of calcium, strontium, barium, potassium, neodymium, cerium, sodium, lithium, cesium, yttrium, lanthanum, samarium, europium, gadolinium, terbium, dysprosium, holmium and ytterbium, said dissolvable magnesium alloy has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

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2. A dissolvable magnesium composite that at least partially forms a ball, a frac ball, a tube, a plug or other tool component that is to be used in a well drilling or completion operation, said dissolvable magnesium composite includes in situ precipitate, said dissolvable magnesium composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said magnesium composite includes greater than 50 wt. % magnesium, said in situ precipitate includes said additive material, said additive material includes one or more metal materials selected from the group consisting of a) copper wherein said copper constitutes 0.1-35 wt. % of said dissolvable magnesium composite, b) wt. % nickel wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium composite, and c) cobalt wherein said cobalt constitutes 0.1-20 wt. % of said dissolvable magnesium composite, said dissolvable magnesium composite has a dissolution rate of at least 75 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

3. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 75-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

4. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 84-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

5. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 100-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

6. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 0.6-1 mg/cm²/hr. in 3 wt. % KCl water mixture at 21° C.

7. The dissolvable magnesium composite as defined in claim 2, wherein said dissolvable magnesium composite has a dissolution rate of 0.5-1 mg/cm²/hr. in 3 wt. % KCl water mixture at 20° C.

8. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and no more than 10 wt. % aluminum, and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese.

9. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and no more than 10 wt. % aluminum, and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.05-1 wt. % zirconium, 0.05-0.25 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

10. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes nickel.

11. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes nickel, said nickel constitutes 0.3-7 wt. % of said dissolvable magnesium composite.

12. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes nickel, said nickel constitutes 7-10 wt. % of said dissolvable magnesium composite.

13. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes copper.

14. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes copper, said copper constitutes 0.5-15 wt. % of said dissolvable magnesium composite.

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15. The dissolvable magnesium composite as defined in claim 2, wherein said additive material includes copper, said copper constitutes 15-35 wt. % of said dissolvable magnesium composite.

16. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium content in said dissolvable magnesium composite is at least 75 wt. %.

17. The dissolvable magnesium composite as defined in claim 2, wherein said magnesium content in said dissolvable magnesium composite is at least 85 wt. %.

18. The dissolvable magnesium composite as defined in claim 2, wherein said additive material is a metal or metal alloy.

19. A dissolvable magnesium cast composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material includes one or more metals selected from the group consisting of a) copper wherein said copper constitutes at least 0.01 wt. % of said dissolvable magnesium cast composite, b) nickel wherein said nickel constitutes at least 0.01 wt. % of said dissolvable magnesium cast composite, and c) cobalt wherein said cobalt constitutes at least 0.01 wt. % of said dissolvable magnesium cast composite, said magnesium composite includes in situ precipitate, said in situ precipitate includes said additive material, a plurality of particles of said in situ precipitate having a size of no more than 50 μ m, said magnesium composite has a dissolution rate of at least 5 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

20. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium composite includes at least 85 wt. % magnesium.

21. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium composite has a dissolution rate of at least 40 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

22. The dissolvable magnesium cast composite as defined in claim 20, wherein said magnesium composite has a dissolution rate of at least 40 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

23. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium composite includes no more than 10 wt. % aluminum.

24. The dissolvable magnesium cast composite as defined in claim 20, wherein said magnesium composite includes no more than 10 wt. % aluminum.

25. The dissolvable magnesium cast composite as defined in claim 21, wherein said magnesium composite includes no more than 10 wt. % aluminum.

26. The dissolvable magnesium cast composite as defined in claim 22, wherein said magnesium composite includes no more than 10 wt. % aluminum.

27. The dissolvable magnesium cast composite as defined in claim 23, wherein said magnesium composite includes at least 50 wt. % magnesium.

28. The dissolvable magnesium cast composite as defined in claim 25, wherein said magnesium composite includes at least 50 wt. % magnesium.

29. The dissolvable magnesium cast composite as defined in claim 19, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

30. The dissolvable magnesium cast composite as defined in claim 20, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

31. The dissolvable magnesium cast composite as defined in claim 22, wherein said dissolvable magnesium cast com-

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posite has a dissolution rate of 40-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

32. The dissolvable magnesium cast composite as defined in claim 23, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

33. The dissolvable magnesium cast composite as defined in claim 27, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

34. The dissolvable magnesium cast composite as defined in claim 28, wherein said dissolvable magnesium cast composite has a dissolution rate of 40-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

35. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

36. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

37. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt. %, zinc in an amount of 0.1-6 wt. %, zirconium in an amount of 0.01-3 wt. %, manganese in an amount of 0.15-2 wt. %, boron in an amount of 0.0002-0.04 wt. %, and bismuth in an amount of 0.4-0.7 wt. %.

38. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt. %, zinc in an amount of 0.1-6 wt. %, zirconium in an amount of 0.01-3 wt. %, manganese in an amount of 0.15-2 wt. %, boron in an amount of 0.0002-0.04 wt. %, and bismuth in an amount of 0.4-0.7 wt. %.

39. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt. %, zinc in an amount of 0.1-3 wt. %, zirconium in an amount of 0.01-1 wt. %, manganese in an amount of 0.15-2 wt. %, boron in an amount of 0.0002-0.04 wt. %, and bismuth in an amount of 0.4-0.7 wt. %.

40. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of 0.5-10 wt. %, zinc in an amount of 0.1-3 wt. %, zirconium in an amount of 0.01-1 wt. %, manganese in an amount of 0.15-2 wt. %, boron in an amount of 0.0002-0.04 wt. %, and bismuth in an amount of 0.4-0.7 wt. %.

41. The dissolvable magnesium cast composite as defined in claim 20, wherein said magnesium alloy includes at least 85 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese.

42. The dissolvable magnesium cast composite as defined in claim 22, wherein said magnesium alloy includes at least 85 wt. % magnesium and one or more metals selected from

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the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese.

43. The dissolvable magnesium cast composite as defined in claim 23, wherein said magnesium alloy includes at least 85 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, 0.01-3 wt. % zirconium, and 0.15-2 wt. % manganese.

44. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese.

45. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and one or more metals selected from the group consisting of 0.5-10 wt. % aluminum, 0.1-2 wt. % zinc, 0.01-1 wt. % zirconium, and 0.15-2 wt. % manganese.

46. The dissolvable magnesium cast composite as defined in claim 27, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.05-1 wt. % zirconium, 0.05-0.25 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

47. The dissolvable magnesium cast composite as defined in claim 28, wherein said magnesium alloy comprises greater than 50 wt. % magnesium and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.05-1 wt. % zirconium, 0.05-0.25 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

48. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium alloy comprises 60-95 wt. % magnesium, 0.5-10 wt. % aluminum, 0.05-6 wt. % zinc, and 0.15-2 wt. % manganese.

49. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium alloy includes 60-95 wt. % magnesium and 0.01-1 wt. % zirconium.

50. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium alloy includes 60-95 wt. % magnesium, 0.05-6 wt. % zinc, and 0.01-1 wt. % zirconium.

51. The dissolvable magnesium cast composite as defined in claim 19, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of 0.1-3 wt. % zinc, 0.01-1 wt. % zirconium, 0.05-1 wt. % manganese, 0.0002-0.04 wt. % boron, and 0.4-0.7 wt. % bismuth.

52. The dissolvable magnesium cast composite as defined in claim 19, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

53. The dissolvable magnesium cast composite as defined in claim 20, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

54. The dissolvable magnesium cast composite as defined in claim 22, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

55. The dissolvable magnesium cast composite as defined in claim 23, wherein said additive material includes nickel, said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

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71. The dissolvable magnesium cast composite as defined in claim 20, wherein said wherein said additive material includes cobalt, said cobalt constitutes 0.1-20 wt. % of said magnesium composite.

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85. The dissolvable magnesium cast composite as defined in claim 25, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

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86. The dissolvable magnesium cast composite as defined in claim 27, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

87. The dissolvable magnesium cast composite as defined in claim 28, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

88. The dissolvable magnesium cast composite as defined in claim 19, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

89. The dissolvable magnesium cast composite as defined in claim 20, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

90. The dissolvable magnesium cast composite as defined in claim 22, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

91. The dissolvable magnesium cast composite as defined in claim 23, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

92. The dissolvable magnesium cast composite as defined in claim 27, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

93. The dissolvable magnesium cast composite as defined in claim 28, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of 14-50 ksi, b) a shear strength of 11-25 ksi, and c) an elongation of at least 3%.

94. A dissolvable magnesium cast composite comprising a mixture of magnesium or a magnesium alloy and an additive material, said additive material includes a) nickel wherein said nickel constitutes 0.01-5 wt. % of said dis-

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solvable magnesium cast composite or b) nickel wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite, said dissolvable magnesium cast composite includes in situ precipitate, said in situ precipitate includes said additive material, said dissolvable magnesium cast composite has a dissolution rate of at least 75 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

95. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium cast composite includes no more than 10 wt. % aluminum.

96. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium cast composite includes at least 85 wt. % magnesium.

97. The dissolvable magnesium cast composite as defined in claim 95, wherein said dissolvable magnesium cast composite includes at least 85 wt. % magnesium.

98. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium cast composite has a dissolution rate of 75-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

99. The dissolvable magnesium cast composite as defined in claim 97, wherein said dissolvable magnesium cast composite has a dissolution rate of 75-325 mg/cm²/hr. in 3 wt. % KCl water mixture at 90° C.

100. The dissolvable magnesium cast composite as defined in claim 94, wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

101. The dissolvable magnesium cast composite as defined in claim 99, wherein said nickel constitutes 0.1-23.5 wt. % of said dissolvable magnesium cast composite.

102. The dissolvable magnesium cast composite as defined in claim 94, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

103. The dissolvable magnesium cast composite as defined in claim 101, wherein said dissolvable magnesium cast composite has one or more properties selected from the group consisting of a) a tensile strength of at least 14 ksi, b) a shear strength of at least 11 ksi, and c) an elongation of at least 3%.

* * * * *

CERTIFICATE OF SERVICE

I certify that on December 8, 2022, the foregoing document was served, via the Court's CM/ECF Document Filing System, upon the following registered CM/ECF users:

David B. Cupar
Matthew J. Cavanagh
Andrew D. Gordon-Seifert

Dated: December 8, 2022

s/Martin S. High

*COUNSEL FOR DEFENDANTS-
APPELLANTS*

CERTIFICATE OF COMPLIANCE

In accordance with Federal Circuit Rule 32(b) and Federal Rule of Appellate Procedure 32(a)(7), Appellants certify that the foregoing complies with the relevant type-volume limitations because it meets one of the following:

- ☒ The filing has been prepared using a proportionally-spaced typeface and includes **12,639** words.
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Dated: December 8, 2022

s/Martin S. High

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